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DAPARTMENT OF NON WOVEN

RELATION BETWEEN NEEDLE AND NEEDLE-LESS ELECTROSPINNING USING POLY (ETHYLENE OXIDE)

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Abstract

This Thesis predict a relation between needle and needle-less electrospinning ,as the needle-less or roller electrospinning is a time consuming and expensive procedure .so Poly (ethylene oxide) with different molecular weight ,concentration and additives was tested on needle and needle-less elctrospinning with changing solution and process parameters (Molecular weight,voltage supply ,distance between electrodes, addition of NaCl-salt) whereas the ambient parameters (temperature and humidity)were kept constant. The results were examined on SEM and shows a great relationship between needle and needle-less electrospinning particularly in terms of spinnability,fiber quality ,non-fiborous area ,fiber diameter, fiber diameter distribution and throughput. The result are usefull in predicting the behavior of polymers in needle-less electrospinning with results from needle electrospinning.

Keywords: Relation between needle and needle-less electrospinning,Poly(ethylene oxide) nanofibers,Electrospinning comparison,roller electrospinning fiber diameter distribution.

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1 Introduction

The use of electric charge to break up liquids into small particles has been well known and extensively studied for over a century. This is true for both electro spraying, in which low viscosity liquids can be atomized into droplets, and electro spinning, in which viscoelastic liquids can be transformed into filaments of nanometer dimensions. With the emergence of nanotechnology, researchers become more interested in studying the unique properties of nanoscale materials. Electrospinning, an electrostatic fiber fabrication technique has evinced more interest and attention in recent years due to its versatility and potential for applications in diverse fields. The notable applications include in tissue enegineering, biosensors, filtration, wound dressings, drug delivery and enzyme immobilization [1]. Using the keyword 'electrospining' for a search on internet will return a thousand scientific papers, but almost all of them concerned on needle electro spinning technique includes many aspects as mechanism of electrospinning, materials for electro spinning, properties of nanofibers, factors effect to spinning process and to products properties .. etc, as summarize by Anthony L.Andrady [2] or Jon Stanger and his co-workers [3]. Up to now, Nanospider is the unique commercial equipment to produce nanofibers web.via needleless electrospinning technology. This equipment, which is first patented by Jirsak [4],enable to produce membranes collected fibers in a range from 100 to 600 nm of diameter.

1.1 History

Electrospinning, thought recently highlighted, is not a new process. It has long history. In the late 1500s William Gilbert set out to describe the behaviour of magnetic and electrostatic phenomena. His work is an early example of what would become the modern scientific method. He had distinguished between the magnetic forces arising from a lodestone (natural magnet) and the electrostatic forces arising from rubbed amber. One of his more obscure observations was that when a suitably charged piece of amber was brought near a droplet of water it would form a cone shape and small droplets would be ejected from the tip of the cone - the first recorded observation of electrospraying. The first description of a process recognizable as electro spinning was in 1902 when J.F.Cooley filed a United States patent entitled "Apparatus for electrically dispersing a fibres". In his patent (US692631) he describes a method of using high voltage power supplies to generate yarn. Even at this early stage it was recognized that to form fibres

rather than droplets the fluid must be sufficiently viscous, solvent volatile enough to evaporate to allow regeneration of the solid polymer, and electric field strength within a certain range.

Bose found, at the very first attempt of investigating this phenomena in 1745 that, under certain conditions, the clouds of atomized droplets is preceded by a jet flow. During 1912-1931 first Burton and Wiegand and then Zeleny and Macky confirmed this flow pattern and investigated it in detail.

The potential of this technique of fiber generation was realized simultaneously by a number of investigators and, in the final analysis, served as the springboard for designing an industrial method of electro spinning of fibrous materials. The first patent for obtaining fibers from a jet of material injected into a space with strong electric field were awarded in 1902 to Morton, but the fibrous layer produced under this patents was too weak for practical use. The first real success was attained in 1930, when Formhols suggested that the fibers be generated from solutions of polymer resins. This method was developed in 1936 by Norton for obtaining fibers from melts and solutions of rubber and other synthetic resins, however, all this patents did not lead to production of usable fibers because of low quality and inability to complete commonly used fibers. A decisive breakthrough in development and application of the electro spinning method was attained in 1938 in the USSR, by young co-workers of Prof. N.A.Fuks (Fuchs).

Theoretically, between 1964 and 1969, Sir Geoffrey Ingram Taylor produced the theoretical underpinning of electro spinning. Taylor's work after a broad career including modeling of turbulent mixing of air at the Arctic, significant contributions to the fields of fluid mechanics and solid mechanics via work on the Manhattan Project and development of supersonic aircraft. Taylor's work contributed to electro spinning by mathematically modeling the shape of the cone formed by the fluid droplet under the effect of an electric field; this characteristic droplet shape is now known as the Taylor Cone. Nowadays, Nano spider is the unique commercial equipment to produce nanofibers-web via needless electrospinning technology. This equipment is first patented by Prof Jirsak from Technical university of Liberec, and then it is developed by Czech company Elmarco, Liberec to enables to use in industrial production of non-woven textiles. This equipment can produce membranes collected fibers in a range from 100 to 600 nm of diameter. Such materials are widely utilized in many fields, as filtration, healthcare, building construction, automotive industries, industry, cosmetics and many others. Elmarco produced the pilot manufacturing line for Nano fiber production in 2004,

and in 2006 offered the first models for industrial production. Recent models of Nanospiders have production rate up to 30 m/min with the fabric width bigger than 1 m.

1.2 Potential applications

Nanofiber related publications and patents appear to have grown in number rapidly over recent years. An analysis of patent activity in particular allows an overall summary of the commercial potential of electro spun Nanofibers and affords the identification of application areas where the technology might play a key role. A large majority of the patents issued on the technology are U.S. patents, with about two-thirds being related to biological or medical application of nanofibers. The second largest group deals with application of nanofibers in filtration, followed by other applications such as sensors, composites, and catalysis. Here is some diversity of applications where nanofibers might be used:

- Tissue engineering scaffolding
    - Porous membrane for skin
    - Tubular shapes for blood vessels and nerve regenerations
    - Three dimensions scaffold for bone and cartilage regenerations
- Applications in life science
    - Drug delivery carrier
    - Wound dressing
- Cosmetic skin mask
    - Skin cleaning
    - Skin healing
    - Skin therapy with medicine
- Military protecting clothing
    - Minimal impedance to air
    - Efficiency in trapping aerosol particles
    - Anti-biochemical gases
- Nano sensors
    - Thermal sensors
    - Piezoelectric sensors
    - Biochemical sensors
    - Fluorescence optical chemical sensors

- Filter media
    - Liquid filtration
    - Gas filtration
    - Molecule filtration
- Other industrial applications
    - Micro/nano electronic devices
    - Electromagnetic interference shielding
    - Photo voltaic devices
    - LCD devices
    - Ultra-lightweight spacecraft materials
    - Higher efficient and functional catalysts

1.3 Principle of electrospinning

Up to now, two popular ways to produce nanofibers using high voltage are known those are needle electrospinning and needle-less electrospinning. The first way has been used popularly by researchers in laboratories. Using the needle electrospinning, spinable polymer solutions are easily spun and controlled to achieve desired products. The second way described above is becoming a commercial technique to produce nanofibers membrane. In the needle electrospinning, there is only one jet per needle and the spinning area is very small (0.5-1 mm^2), whereas in the needle-less electrospinning, there is a number of jets, usually 3,000 – 45,000 jets per one square meter of the surface of spinning roller electrode. There are some other considerable differences between these two ways to produce nanofibers such as scope of properties of spinnable polymer solutions, factors affecting the spinning process and product properties, etc. Two figures(Fig1,Fig2) below show schematic diagram of needle and needle-less apparatuses.

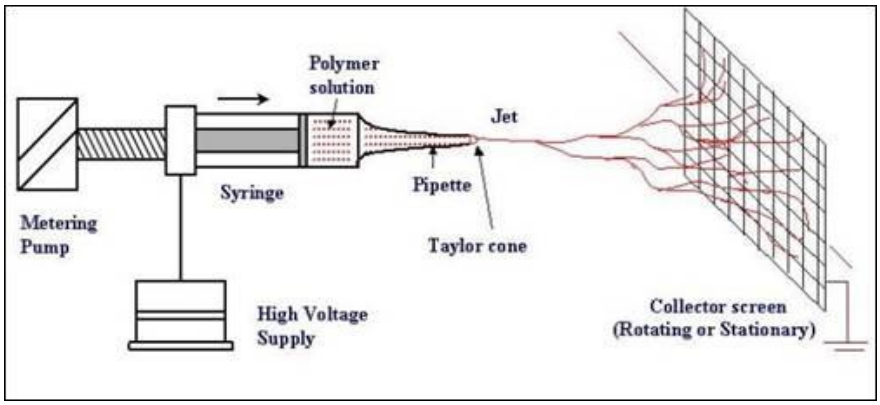


Figure 1 Schematic diagram of needle electrospinning

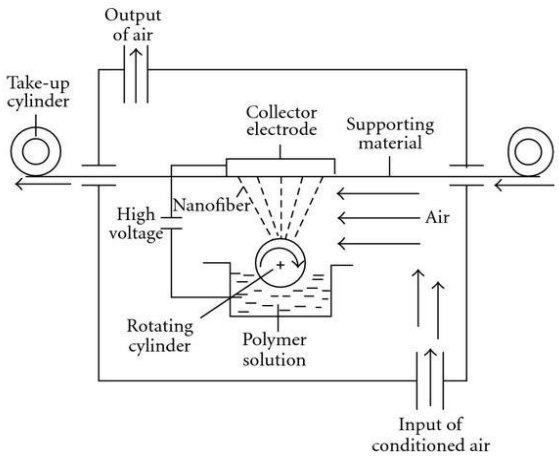


Figure 2 schematic diagram of needleless apparatuses

Schematic diagram of a needle electro spinning device is shown in Fig.1 [3]. It consists of a syringe, hollow needle, feeding mechanism, a grounded collector electrode and a supply of high voltage. Charged solution of polymer is fed through the hollow needle. Due to electric field, Taylor cone is created at the tip of hollow needle. A polymer jet moves out of the tip of Taylor cone which is subsequently converted into submicron fibers. In needleless (roller) electro spinning (schematic diagram in Fig.2), a slowly rotating roller partially is immersed in polymer solution. Polymer solution is connected to a high voltage source. Collector is usually grounded. In electro spinning process, polymer solution is taken to the surface of the roller because of its rotation. With suitable high voltage, many Taylor cones are simultaneously created on the roller surface, and produce nanofibers. The nanofibers are then transported towards the collector [5]. Two presented devices seem to be different, nevertheless they are based on the same electrospinning mechanism. The mechanism consists in a war between electrostatic and capillary forces [6]. This phenomenon has been described in detail by Lukas and his co-workers in [6]. Following that, the electrostatic force comes from charged liquid bodies that content a huge number of ions of the same sign. The material is pulled to the oppositely charged or grounded electrode by Coulombic forces. Simultaneously, repulsive forces inside polymer solution lead to formation of nanofibers (or small particles). The other force, capillary force cause the liquid particles to flock together to minimize the liquid surface area and surface energy. Electrospinning process can be divided into three stages.

In the first stage, polymer solution is fed by roller from container or by pump in the needle spinning process. High electric potential inserted in the solution leads to the formation of jets. The jets (jet) are discharged from roller's surface or from droplet on needle tip. This causes the jets to steadily accelerate and thin out along an axis aligned with the general direction of electric field. This is an important stage because the stability and results of it controls all its subsequent stages and, in the final analysis, the desired properties of the finished fiber.

The second stage consists of several simultaneously occurring processes. In it, the fluctuations of the electric lines of force, caused by time and space variation of the bulk density of electrical charges, causes jets to turn transversely to the field direction and to be decelerated by the constantly increasing drag force of the gas. This produces a cloud that expands toward the collector by action of same polarity charges. At the same time, the rate of vaporization of the solvent that started already at the first stage of the process is steeply intensified, the jet solidifies and the resulting fibrous cloud drifts in the applied electric field onto collector. At this stage the jet may still undergo a sequence of splitting resulting in the formation of an unsteady bulk fiber-mesh structure.

The following, third stage also consists of two simultaneous processes: the first consisting of random deposition of fibers into a layer on collector and the second of a gas spark discharge between collector and the fiber layer forming on it,that closes the electric circuit.

1.4 Aim of the work

Needleless electro spinning is a quite new technique.as it is expensive and time consuming process so the objective of this work is to find some type of relationship between needle and needle-less electro spinning so that it can be easily predicted by the results of needle electro spinning which is comparatively cheap and time saving process. The central point of experimental work will be to test poly ethylene oxide with different molecular weight, polymer concentration and additives, etc.with changing solution and process parameters(Molecular weight, voltage supply, distance between electrodes, addition of NaCl-salt)whereas the ambient parameters(temperature and humidity) were kept constant. The result will be examined on SEM to find relationship between Needle and Needle-less electrospinning particularly in terms of spinability, throughput, fiber quality, fiber diameter, non-fibrous area and fiber diameter distribution.

2 Theoretical part

2.1 Viscosity of polymer solutions

Solution viscosity depends on the nature of polymer, its molecular weight, concentration of the solution and the temperature. Viscometry is therefore a convenient practical experimental method to determine an average viscosity molecular weight $\overline{M}_v$ of polymers. Despite the experimental simplicity of viscometry the viscosity-average molecular weight is invariably solvent dependent. It less precise than the averages, $\overline{M}_n$ or $\overline{M}_w$,determined by other methods. Most polymers are reported to be electrospun from solution - a solution of high enough viscosity is essential to obtain continuous electrostatic spinning (as opposed to electrospraying).

For simple low-molecular weight liquids, the linear equation applies at constant temperature. Polymer solutions generally do not fall into this category of Newtonian liquids. At moderate shear rates polymer solutions generally show reduced viscosity or undergo shear-thinning. Fig3 compares the shear rate dependence of viscosity for a Newtonian liquid and a non-Newtonian polymer solution. At very high shear rates, however, a non- Newtonian liquid may revert to Newtonian behavior.

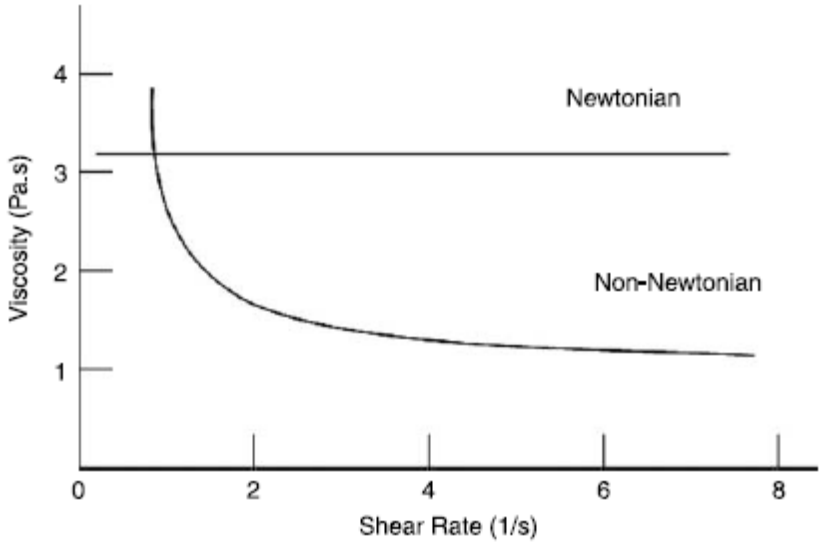


Figure 3 viscosity dependency on the shear rate for a Newtonian liquid and a non-Newtonian polymer solution.

2.2 Parameters in needle electrospinning

In this section, the author will concern on effects of various parameters on needle electro spinning. There are extraordinary many variables influencing the electro spinning process as well as product properties. These can be divided into two big groups as follows:

- Material parameters: additives, molecular weight of polymer, concentration, viscosity, conductivity, molecular weight, and surface tension etc.
- Process parameters: include applied electric field, distance between electrodes, feeding rate. Each of these parameters influences the spinning process and the product properties.[53]

2.2.1 Material parameters

2.2.1.1 Concentration

Many studies show that to obtain fibers via electrospining, the concentration of solution cannot be too low. Via needle spinning, with low concentration of solution, the product includes beads and fibers. The shape of beads changes from spherical to spindle-like and finally uniform fibers with increased diameters by increasing concentration of solution [8-13]. On the other hand, if concentration of solution is too high, spinning process is difficult because of high viscosity and produced fibers show great diameters. Thus, the optimum concentration of polymer solution should be found for electro spinning process [14]. Researchers also found relationship between solution concentration and fiber diameter as a power law relationship, that increasing concentration of solution, increases the fiber diameter [10, 15].

2.2.1.2 Molecular weight

Some solution properties such as viscosity and in some extent also surface tension, conductivity and dielectric strength are significantly affected by molecular weight of polymer [13]. And of course, it also affect to electro spinning process and morphology of fibers. Generally, electro spinning can only occur with moderately concentrated solutions, as the process of jet formation relies on the entanglement of polymer chains [12, 16, 17].Two approaches that address the relationship between the concentration regime and electrospinability of polymer solutions have been proposed. Both can

potentially identify concentration regimes where defect-free continuous nanofibers can electro spun

2.2.1.3 Viscosity

In electrospinning, solution viscosity is an important factor determining whether the process occurs or not; it also has significantly relationship to fibers diameter and morphology of products. If the viscosity is too low, the solution cannot spin because of no continuous fiber is formed; conversely, if the viscosity is too high, it is difficult to eject jets from polymer solution. So determining a suitable range of viscosity for each kind of polymer to use as material in electro spinning is necessary [19]. Fong and his co-workers [20] have studied polyethylene oxide (PEO) to study nanofiber formation in different viscosities, and the results show that the viscosity range of PEO, which is suitable for electrospinning, is between 1 to 20 poise. It is obvious that the solution viscosity is strongly related to the concentration of the solution and the relationship between solution viscosity or polymer concentration and the fibers obtained from electrospinning has been studied in a numbers of systems, including poly (ethylene oxide) (PEO) [22,23]; poly (vinyl alcohol) (PVA)[5] .At very high viscosity polymer solutions usually show longer stress relaxation times, which could prevent the fracturing of the ejected jets during electrospinning, An increase in solution viscosity or concentration gives rise to a larger and more uniform fiber diameter[7].

2.2.1.4 Surface tension

Surface tension, more likely to be a function of solvent compositions of the solution plays a critical role in the electro spinning process and by reducing the surface tension of a nanofiber solution fibers can be obtained without beads. Different solvents may contribute to different surface tensions. Generally, high surface tension of a solution inhibits the electrospinning process because of instability of the jets and the generation of sprayed droplets[18]. The formation of droplets, beads and fibers depends on the surface tension of solution. Lower surface tension of the spinning solution helps electro spinning to occur at a lower electric field [14]. However, not necessarily a lower surface tension of a solvent will always be more suitable for electrospinning. Basically, surface tension determines the upper and lower boundaries of the electrospinning window if all other variables are held constant [7,10].

2.2.1.5 Conductivity/surface charge density

Polymers are mostly conductive, with a few exceptions of dielectric materials, and the charged ions in the polymer solution are highly influential in jet formation. Solution conductivity is mainly determined by the polymer type, solvent used, and the presence of ionisable salts. It has been found that with the increase of electrical conductivity of the solution, there is a significant decrease in the diameter of the electrospun nanofibers whereas with low conductivity of the solution, there results insufficient elongation of a jet by electrical force to produce uniform fibers, and beads may also be observed. Hayati [11] have showed that highly conductive solutions are extremely unstable in the presence of strong electric fields, which results in a dramatic bending instability as well as a broad diameter distribution. Generally, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity and it has been found that the there is drop in the size of the fibers is due to the increased electrical conductivity. It was observed that the jet radius varied inversely with the cube root of the electrical conductivity of the solution [9],[11-14]. Natural polymers are generally polyelectrolytic in nature, for example, gelatin. The ions increase the charge carrying capacity of the jet, thereby subjecting it to higher tension with the applied electric field. Thus the fiber forming ability of the gelatin is less as compared to the synthetic ones. Zong [13] have demonstrated the effect of ions by adding ionic salt on the morphology and diameter of electrospun fibers and found that with the addition of ionic salts like KH_2PO_4, NaH_2PO_4, and NaCl it produced beadless fibers with relatively smaller diameters ranging from 200 to 1000 nm. This approach of increasing the solution conductivity by the use of salt addition has also been used for other polymers such as, collagen type I-PEO[18], PVA[8], polyacrylic acid (PAA)[14], polyamide-6 [15] and others. With the use of salts, the uniformity of fibers increases and there is a decrease in beads generation.

2.2.2 Process parameters

2.2.2.1 Applied voltage

Applied voltage is the most important parameter in the electro spinning process. It supplies whole energy for spinning system. Without applied voltage, the spinning process cannot occur. Many researchers have studied the effects of applied voltage to spinning process and nanofibers properties. There is a little dispute about the behaviour

of applied voltage in the e1ectrospinning process and properties of nanofibers. Reneker and his co-workers [28] have showed that there is not much effect of dielectric field on the fiber diameter with electrospinning of polyethylene oxide. Researchers have suggested that when higher voltage are applied, there is more polymer ejection and this facilitates the information of a larger diameter fiber [29, 30]. Other authors have reported that an increase in the applied voltage(i.e., by increasing the electric field strength), increases the electrostatic repulsive force on the jet which ultimately favours the narrowing of fiber diameter. In most cases, a higher voltage cases greater stretching of the solution due to the greater columbic forces in the jet as well as a stronger electric field and these effects lead to reduction in the fiber diameter and also rapid evaporation of solvent from the fibers results. At a higher voltage there is also greater probability of beeds formation [8, 13]. Similar behaviour of applied voltage on fiber diameter is also researched by Larrondo and Manley [31-33]. They have showed the decrease of fiber diameter by roughly halfby doubling the applied electric field. Thus, voltage influences fiber diameter, but the level of significance varies with the polymer solution concentration and on the distance between the tip and the collector [34].

2.2.2.2 Feed rate/Flow rate

The feed rate of the polymer solution from the syringe is an important process parameter via needle electro spinning because of its effects to the jet velocity and the material transfer rate. A lower feed rate is more desirable as the solvent will get enough time for evaporation [35]. There should always be a minimum flow rate of the spinning solution. It has been observed that the fiber diameter and the pore diameter increases with an increase in the polymer flow rate in the case of polystyrene (PS) fibers and by changing the flow rate, the morphological structure can be slightly changed. Few studies have systematically investigated the relationship between solution feed or flow rate on fiber morphology and size [26]. High flow rates result in beaded fibers due to unavailability of proper drying time prior to reaching the collector [35-37].

2.2.2.3 Types of collectors[53]

One important aspect of the electrospinning process is the type of collector used. In this process, a collector serves as a conductive substrate where the nanofibers are collected. Generally, aluminium foil is used as a collector but due to difficulty in transferring of

collected fibers and with the need for aligned fibers for various applications, other collectors such as conductive paper, conductive cloth, wire mesh [38], pin [39], parallel or grid bar [40], rotating rod, rotating wheel [41], liquid non solvent such as methanol coagulation bath [42] and others are also common types of collectors nowadays. In the blowing-assisted electro spinning of hyaluronic acid, Wang [38] used two kinds of collector aluminium foil and wire screen and found that a less conductive area of wire screen imposes a negative effect on fiber collection. With less conductive area, there was generation of beaded fibers because of the less surface area. In another study they compared wire screen with aluminium foil and wire screen without aluminium. foil in the same conductive area and found that pure wire screen is a better collector for fiber collection because with the use of wire screen the transfer of fibers to other substrates became easy. The fiber alignment is determined by the type of the target/collector and its rotation speed [43]. The generated nanofibers are deposited on the collector as a random mass due to the bending instability of the highly charged jet [44, 45]. Several research groups have demonstrated the use of a rotating drum or a rotating wheel-like bobbin or metal frame as the collector, for getting aligned electrospun fibers more or less parallel to each other [8]. Several types of split electrodes have been used for getting aligned nanofibers and typically such collectors consist of two conductive substrates separated by a void gap where aligned nanofibers are deposited [46-49].

2.2.2.4 Tip to collector distance

The distance between the tip and the collector has been examined as another approach to control the fiber diameters and morphology. It has been found that a minimum distance is required to give the fibers sufficient time to dry before reaching the collector, otherwise with distances that are either too close or too far, beads have been observed [30]. The effect of tip and the collector distance on fiber morphology is not as significant as other parameters and this has been observed with electrospinning of PVA[52], gelatin [51]and chitosan [30] .It has been reported that flatter fibers can be produced at closer distances but with increase in distance rounder fibers have been observed with the spinning of silk-like polymer with fibronectin functionality[57]. For polysulfone, closer distances between the tip and collector has yielded smaller fibers[10]. One important physical aspect of the electrospinning nanofibers is their dryness from the solvent used to

dissolve the polymer[29]. Thus, there should be optimum distance between the tip and collector which favours the evaporation of solvent from the nanofibers.

2.2.2.5 Ambient parameters

Studies have been conducted to examine the effects of ambient parameters (i.e., temperature and humidity) on the electrospinning process. Mit- Uppatham [54] have investigated the effect of temperature on the electrespinning of polyamide-6 fibers ranging from 25 to 60 *DC* and found that with increase in temperature, there is a yield of fibers with decreased fiber diameter, and they attributed this decline in diameter to the decrease in the viscosity of the polymer solutions at increased temperatures. There is an inverse relationship between viscosity and temperature. The variation in humidity while spinning polystyrene solutions has been studied and shows that by increasing humidity there is an appearance of small circular pores on the surface of the fibers; further increasing the humidity leads to the pores coalescing [55]. It has been found that at very low humidity, a volatile solvent may dry out rapidly as the evaporation of the solvent is faster. Sometimes the evaporation rate is so fast than compared to the removal of the solvent from the tip of the needle and this would create a problem with electro spinning. As a result, the electrospinning process may only be carried out for a few minutes before the needle tip is clogged [25]. It has also been suggested that the high humidity can help the discharge of the electro spun fibers [40]. Hence, apart from solution and the others processing parameter, ambient parameters also affect the electro spinning process.

2.2.3 Summarization of needle electrospinning

From discussions above, and as discussed by Tuan [53]we now can classify the parameters of needle electrospinning into two groups: independent parameters and dependent parameters as in Table1 Table2

Table 1 Parameters of needle electrospinning[53]

Independent Parameters	Dependent Parameter
concetraton of polymer solution [%]	Fiber Diameter [nm]
molecular weight of polymer [g/mol]	Number of Beads
Viscosity of polymer solution [Pas]	Size of beads [nm^2]
Surface tension of solution [mN/m]	length of jet[m]
Applied voltage [KV]	
Feed rate [ml/hour]	
Distance between electrodes [mm]	
Relative humidity [%]	
Temperature [^{0}C]	

Table 2 Effects of needle electro spinning parameters[53]

Independent Parameters	Effect on Dependent Parameter
Applied voltage	Decrease in fiber diameter with increase in voltage
Distance between tip and collector	generation of beads ,moderate distance required for uniform fibers
Feed Rate	Decrease in fiber diameter with decrease in flow rate,generation of beads with too high flow rate
Temperature	Increase in temperature result in decrease in fiber diameter
Solution Parameter	
Viscosity	Increase in fiber diameter with increase of viscosity
Polymer concentration	Increase in fiber diameter with increase of concentration
molecular weight of polymer	reduction in number of beads and droplets with increase of molecular weight
Conductivity	decrease in fiber diameter with increase in conductivity

2.3 Polyethylene oxide

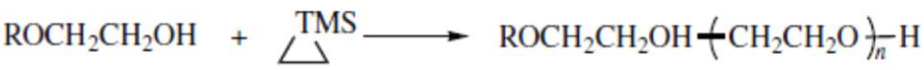
PEO is a non-ionic ,with high molecular weight and good water solubility and heat formative. PEO is characterized with flocculent, thickening ,lubrication, dispersing, fiber and water retention, it can be applied to industries like medicine,fertilizer,pulps, ceramics,detergent, cosmetics,heat treatment,water treatment, fire fighting and oil exploration etc. It is non-toxic,non-irritant, and it will not generate residue,sediment and vaporous elements. Its application fields are widely expanded with the development of the new products and its excellent characteristics are gaining more attention from the numerous R&D organizations.[56]

Ethylene oxide was first prepared in 1859 by Wurtz. Ethylene oxide (C_2H_4O) is a colorless gas that condenses at low temperatures into a mobile liquid. It is miscible in all proportions with water, alcohol, ether, and most organic solvents.

Polymerization[56]

The reaction of ethylene oxide with a nucleophile introduces the hydroxyethyl group:

The product of this reaction can also react with ethylene oxide; if this process is repeated many times, a polymer is formed:



Low molecular weight polymers of ethylene oxide, poly(ethylene glycol), are formed by allowing ethylene oxide to react with water or alcohols under the proper conditions . The average molecular weight can be varied from 200 to 14,000for poly ethylene glycol, whereas the PEO are considered having molecular mass above 20,000 g/mol. While PEG and PEO with different molecular weights find use in different applications and have different physical properties (e.g., viscosity) due to chain length effects, their chemical properties are nearly identical. Different forms of PEG are also available dependent on the initiator used for the polymerization process

Polyethylene oxide or high-molecular polyethylene glycol is synthesized by suspension polymerization. It is necessary to hold the growing polymer chain in solution in the course of the polycondensation process. The reaction is catalyzed by magnesium-, aluminium-, or calcium-organoelement compounds. prevent coagulation of polymer chains from solution, chelating additives such as dimethylglyoxime are used.[56]

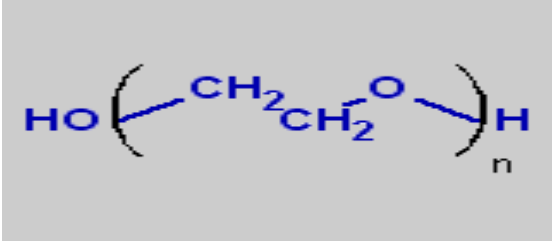


Figure 4 Polyethylene oxide formula[56]

2.4 Needleless electrospinning

In contrast to the needle electro spinning technique, many parameters of needleless electro spinning have not yet been defined. Up to now, not many researchers studied this technology. The parameters of the needleless electrospinning technique are defined by Tuan[53]. Some of them are similar to the parameters of needle electrospinning techniques, some of them are completely new.

These parameters are separated into two groups: independent parameters which can be adjusted and controlled and dependent parameters which depend on independent parameters.

2.4.1 parameters[53]

2.4.1.1 Solution parameters

In common, solution parameters as shown above, are important in the both techniques to produce nanofiber, needle and needleless electrospinning, are similar. In the needle less electrospinning, the optimum parameters must be found in narrower intervals than in needle electro spinning. It means that if the polymer solution can spin in needleless technique it is certainly spinnable on needle technique.

The reason for this difference consists mainly in the high charge density at the tip of hollow needle when compared with that at the big surface of spinning roller electrode.

2.4.1.2 Process parameters

2.4.1.2.1 Applied voltage

Similarly to needle electro spinning technique, applied voltage supply energy for the spinning system. A high voltage is connected to spinning solution through a metal spinning roller. The effects of applied voltage on needleless technique are similar to needle technique as shown in part. Nevertheless, there is a considerable difference between both the techniques in area of spinning electrode which is much bigger in the roller spinning. This big charged area cause much lower field strength in needleless electrospinning process. And this is the reason why the applied voltage in needleless technique must be too much higher values than in the needle technique in case of the same spin able polymer solution.

2.4.1.2.2 Velocity of rotating cylinder

The rotating cylinder has the same mission as the pump in needle technique that supplies polymer solution. The velocity of rotating cylinder will determine amount of solution taken from the tank and applied to spinning area. It also relates to the thickness of solution layer on cylinder. Of course this thickness will depend on viscosity of polymer solution, on temperature ... etc., but normally, in the same conditions, the higher velocity of rotating cylinder the thicker is the layer of polymer solution and the greater amount of solution has been supplied for spinning

2.4.1.2.3 Collector

As described above, needleless technique is quite new, so the collector used in this technique is usually quite simple up to now. That includes a flat rectangle of metal which is grounded and a running fabric which is moving along it collecting nanofibers on its surface. Other types of collector electrodes are being developed and tested, such as cylinders, wires, and others, but this is not the subject of study in this work.

2.4.1.2.4 Distance from rotating cylinder to collector

Similar to needle technique, distance from rotating cylinder to collector will determine spinning space, in which some processes in spinning process occurs as elongation, evaporation, discharged process, ... etc. Similarly to applied voltage, this distance will strongly affect the field strength of spinning space.

2.4.1.2.5 Velocity of running collector fabric

In spinning process via needleless technique, a collector fabric is running through the spinning space, along the collector electrode, to collects nanofibers. The velocity of this fabric (in meters per minute) influences the area weight of nanofiber layer. This also affects to quality of nanofibers membrane as non-fibrous area. Those parameters will be defined later in following sections.

2.4.1.2.6 Ambient parameters

Similarly to needle electro spinning, ambient parameters such as humidity and temperature affect the needle less electro spinning process. The effects are more dominant in needleless electrospinning when compared with needle electrospinning.[53]

2.4.1.3 Density of cones

In contrast with the needle technique, which only has one Taylor cone during spinning process, in needleless technique a number of Taylor cones (N) appear on spinning area during spinning process.

2.4.1.4 Fiber diameter

Similar to the parameter of needle electro spinning, fibers diameter of needleless electro spinning is important parameter to evaluate the quality of nanofibers membrane. The method to determine this parameter is the same to both products of needle and needleless electrospinning. The formula Shows the way to calculate the value of this parameter.

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \qquad \text{..... EQUATION (1)}$$

d_i is fibre diameter or size of bead

n_i is number of elements of the group d,

A_n is number average (fibers diameter or size of beads)

2.4.1.5 Spinning performance (SP)

Spinning performance or throughput is one of the most important characteristics of needle less electrospinning. It describes the amount of nanofiber material produced by the specific spinning device full time. In contrast with the needle electro spinning, the spinning performance is a dependent variable in needleless electro spinning. It can be determined from the mass of nanofibers produced in one minute

and recalculated per one meter long roller spinning electrode. In praxis, spinning performance is recalculated from area weight of produced nanofiber layer as follows:

where SP is spinning performance or throughput, it has unit as g/min/m.

$$SP = \frac{G.v.l_f}{l_r} \quad , \qquad \text{[g/min/m] .....equation (2)}$$

G is weight of nanofibers membrane per area in g/m^2

v is velocity of running collected fabric, in mlmin.

l_f is the width of nanofibers membrane on collected fabric, in m.

l_r is the length of spinning roller, in m.

2.4.2 Non-fibrous area (NFA)

2.4.2.1 Definition

This is another important property of nanofibers membrane. From this value the quality of nanofiber membrane can be estimated. Simultaneously, the NFA value refers to the quality of the spinning process. The NFA is the area fraction of non-fibrous area in membrane to total area of product. It is expressed as percentage, or dimensionless. This can be calculated according to formula

below:

$$NFA = \frac{Total\ non\ fiborous\ area}{total\ area\ of\ nanofiber\ memberane} * 100 \quad [\%] \quad \text{equation(3)}$$

Method to measure:

To measure non-fibrous area, SEM pictures of product will be taken. From these pictures, we can measure the non-fibrous area on surface of sample (see figure 5). Then measure total area of sample. And then use formula (3) to calculate non-fibrous area.

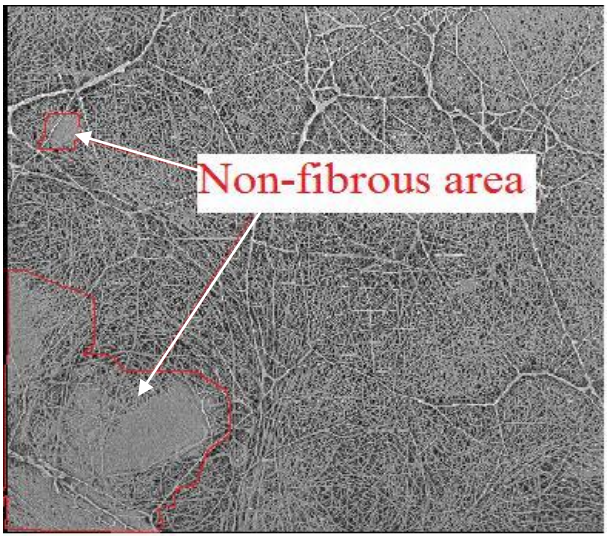


Figure 5 Non-fibrous area[53]

2.4.3 Fibers diameter distribution

The difference in fibers diameter or fibers diameter distribution can be shown by the fraction of groups of diameter or in deviation value. The smaller of deviation the bigger number of the nanofibers had their diameter closes to the others. The standard deviation can be calculated using

the formula in equation (4) and equation (5):

$$\sigma = \sqrt{\frac{1}{N}\sum_{1}^{N}(x_i - \mu)^2} \quad \text{.....equation (4)}$$

σ is standard deviation

N is number elements (measured nanofibers)

x_i is nanofiber diameter

μ is Average nanofibers diameter

$$\boldsymbol{\mu} = \frac{\mathbf{1}}{\boldsymbol{N}} \sum_{\mathbf{1}}^{\boldsymbol{N}} \boldsymbol{x}_{\mathbf{i}} \quad \text{equation (5)}$$

2.4.4 Parameter List

From discussions above, we now can classify the parameters into two groups: independent parameters and dependent parameters as in the table below:

Table 3 Summarization of electro spinning parameters [53]

Independent Parameters	Effect on Dependent Parameter
Concentration of polymer [%]	density of cones (m-2) [A]
molecular weight of polymer (g/mol)	Throughput (g/min/m)
Viscosity of polymer solution (Pas)	Non-Fiborous area (%) [A]
Surface tension of solution (mN/m)	Fiber diameter (nm)
Applied Voltage (kV)	Fiber diameter distribution [A]
Velocity of Cylinder (rpm)	
Distance between electrodes (mm)	
Velocity of collected fabric (m/min)	
Relative humidity (%)	
Temperature (°C)	

3 Experimental Part

This chapter describes materials and methods used in the experiments focused on relations between selected independent and dependent parameters of needle and needleless electro spinning using Polyethylene oxide.

- Firstly PEO with Molecular weight 100,000g/mol 400,000g/mol and 900,000g/mol from ALDRICH company were taken and solutions of different concentrations are made in water solvent.
- Needle electro spinning is done with changing parameters like voltage, distance from collector plate, syringe pump speed and concentration of solution, whereas temperature and relative humidity are kept constant.
- The polymer samples were then tested on needleless elcrospinning with changing parameters of voltage, distance from collector, speed of roller and speed of fabric on which nanofibers are laid whereas temperature and relative humidity are kept constant.
- Different amount of NaCl-Salt(ALDRICH quality p.a) is added and polymer solutions are then tested on needle and needle less electrospinning.
- Deionized distilled water is taken to make solution.
- Results are evaluated with the pictures from electron microscope ,which is then observed on image analysis software to detect the fiber diameter and non-fibrous area.
- Observations and calculations are done to make a comparison between needle and needle-less electro spinning regarding,conductivity,viscosity,surfacetension, fiber quality, throughput, non-fibrous area and effect of NaCl-Salt,fiber diameter and fiber diameter distribution.

3.1 Method

Before electrospinning, some properties of solutions have been measured such as viscosity,surface tension and conductivity .Surface tensions of solutions were measured by Kruss apparatus using plate method. The conductivities of solutions were measured by conductivity meter OK-102/1 branded Radelkis and viscosity were measured on ROTOVISCO RV1.

3.2 Experiments and used materials

3.2.1 PEO of various molecular weights and concentration

PEO is a water soluble synthetic polymer, in this work PEO produced from company ALDRICH is used .PEO samples of different molecular weight and concentration were taked in to experiment.The concentration of solution were choosen so that they cover similar range of viscosity.

Table 4 polymer used for experiment

polymer solutions	M.Wt [g/mol]	Concentration [%]	NaCl-Salt percentage [%]
Polyethelene oxide	100,000	15	-
Polyethelene oxide	100,000	15	1
Polyethelene oxide	100,000	18	-
Polyethelene oxide	100,000	18	1
Polyethelene oxide	400,000	4	-
Polyethelene oxide	400,000	4	1
Polyethelene oxide	400,000	5	-
Polyethelene oxide	400,000	5	1
Polyethelene oxide	400,000	6	0
Polyethelene oxide	400,000	6	0.1
Polyethelene oxide	400,000	6	0.3
Polyethelene oxide	400,000	6	0.5
Polyethelene oxide	400,000	6	1
Polyethelene oxide	400,000	6	1.5
Polyethelene oxide	400,000	6	2
Polyethelene oxide	900,000	2	-
Polyethelene oxide	900,000	2	1
Polyethelene oxide	900,000	3	-
Polyethelene oxide	900,000	3	1

3.2.2 Parameters of Needle Electrospinning

Table 5 PEO Voltage parameter for Needle spinning

15KV	20KV	25KV	30KV

Table 6 PEO Needle to Ground plate distance parameter

Distance of needle from ground plate (cm)											
12	14	16	18	20	22	24	26	28	30	32	34

Table 7 PEO PUMP SPEED parameter:

SPEED OF NEEDLE PUMP (ml/hour)										
0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6
2.8	3.0	3.2	3.4							

3.2.3 Parameters of Needle-less Electrospinning

Table 8 Parameters of Needle-less Electrospinning

Roller length (mm)	145
Roller diameter (mm)	20
Roller angular velocity (rpm)	7
Distance between electrodes (mm)	200
Source voltage (kV)	80
Relative humidity (%)	25
Temperature (^{0}C)	25

4 Results

This chapter shows results of the experiments from chapter 4. The results were shown in tables and in graphs form. They include properties of the solutions viscosity, conductivity ,NaCl-Salt concentration and surface tension ,throughput ,fiber diameter and fiber diameter distribution for both needle and needle-less electrospinning.

4.1 The solutions properties

This section shows some base properties of the PEO solutions as viscosity, conductivity and surface tension.

4.1.1 Polymer Viscosity

Table 9 Zero shear viscosity of Sample solutions

polymer solutionat 25°C	Zero shear viscosity [Pa.S]
PEO 100,000g/mol 15%conc 0%salt	0.32
PEO 100,000g/mol 15%conc 1%salt	0.35
PEO 100,000g/mol 18%conc 0%salt	0.58
PEO 100,000g/mol 18%conc 1%salt	0.59
PEO 400,000g/mol 4%conc 0%salt	0.38
PEO 400,000g/mol 4%conc 1%salt	0.40
PEO 400,000g/mol 5%conc 0%salt	0.63
PEO 400,000g/mol 5%conc 1%salt	0.65
PEO 400,000g/mol 6%conc 0%salt	1.23
PEO 400,000g/mol 6%conc 1%salt	1.40
PEO 900,000g/mol 2%conc 0%salt	0.10
PEO 900,000g/mol 2%conc 1%salt	0.12
PEO 900,000g/mol 3%conc 0%salt	0.38
PEO 900,000g/mol 3%conc 1%salt	0.4

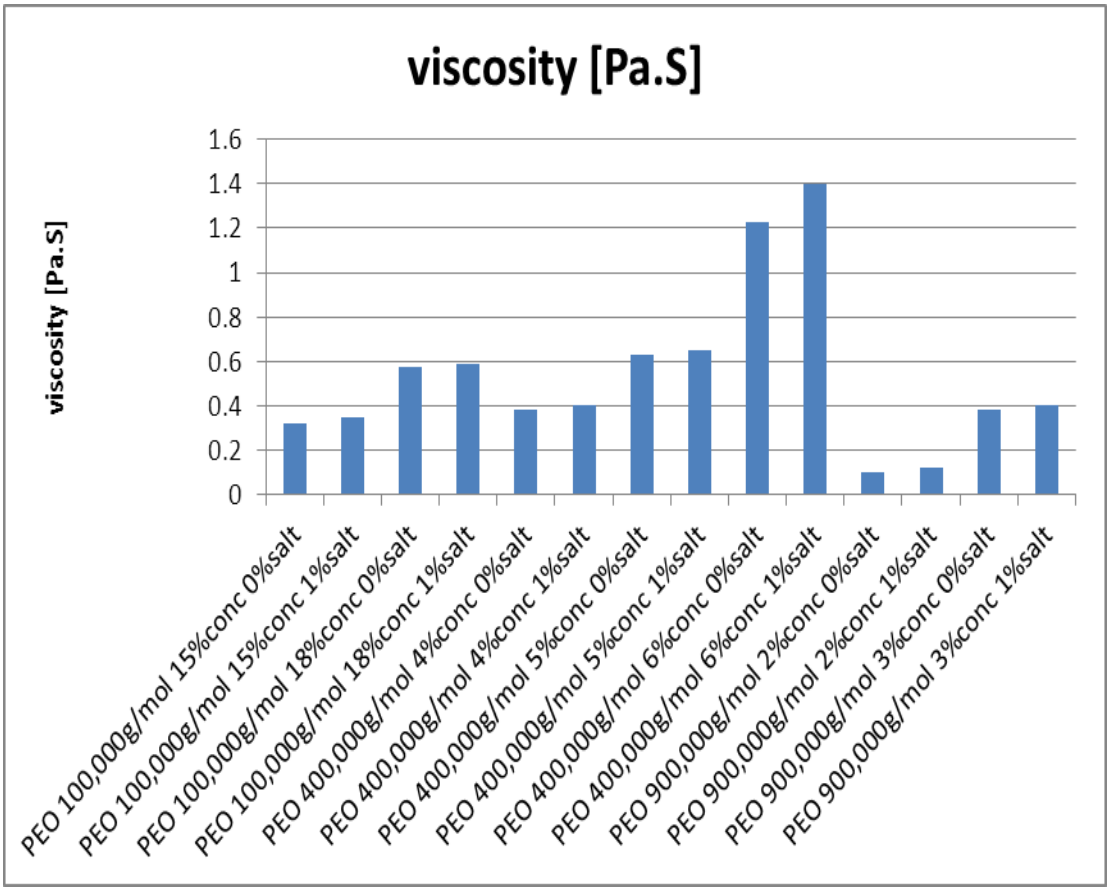


Figure 6 Polymer zero shear Viscosity graph

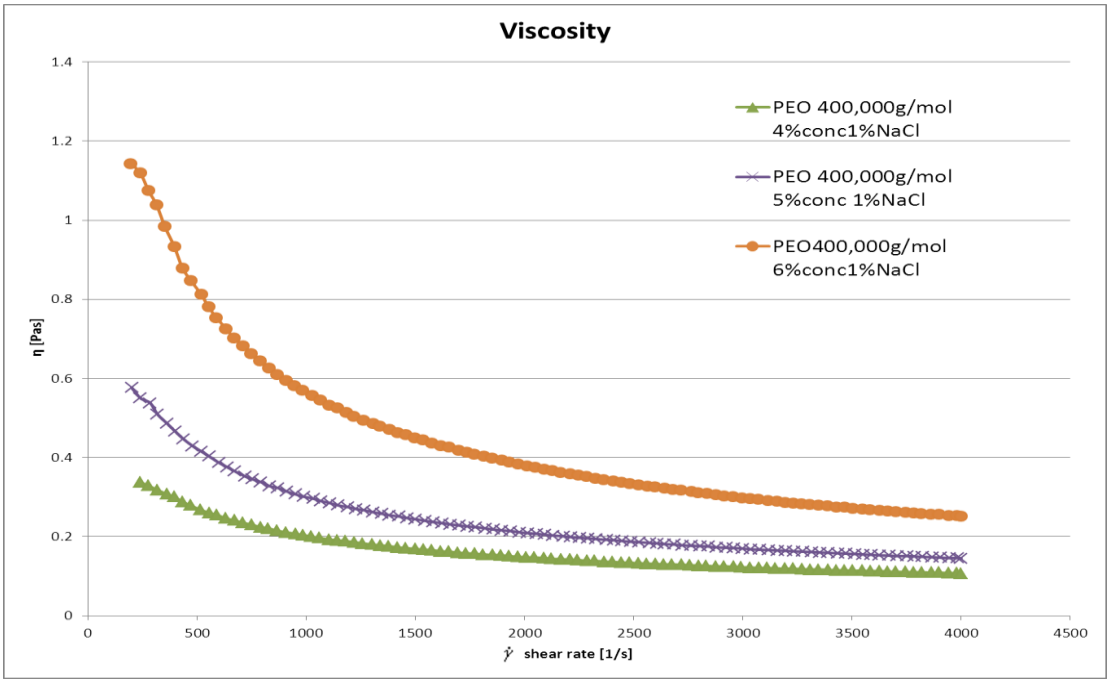


Figure 7 Shear Viscosity graph

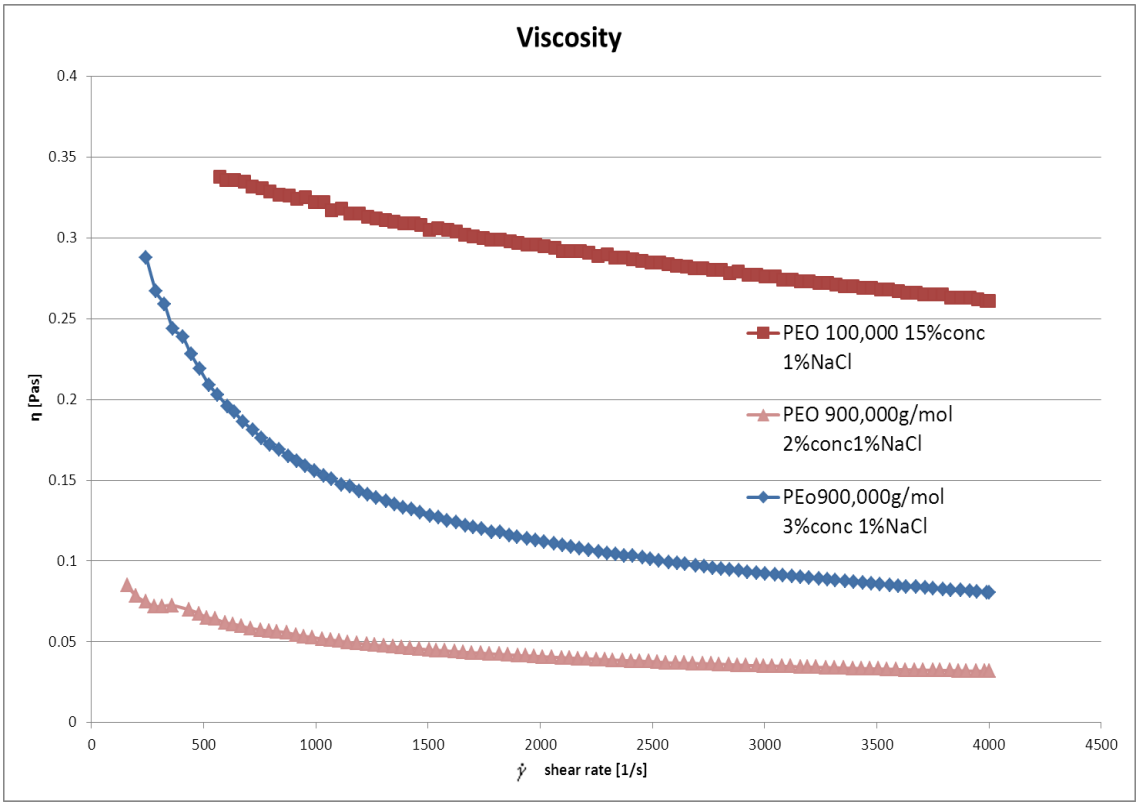


Figure 8 Shear viscosity graph2

4.1.2 Polymer Conductivity

Table 10 Polymer Conductivity

Polymer	conductivity [mS/cm]
PEO100000 g/mol 15% without NaCl-Salt	0.016
PEO100000 g/mol 15%conc, with 1%NaCl-Salt	1.08
PEO100000 g/mol 18%conc. Without NaCl-Salt	0.016
PEO100000 g/mol 18%conc. With 1%NaCl-Salt	1.16
PEO400000 g/mol 4%conc. Without NaCl-Salt	0.016
PEO400000 g/mol 4%conc. With 1% NaCl-Salt	1.56
PEO400000 g/mol 5%conc. Without NaCl-Salt	0.016
PEO400000 g/mol 5%conc. With 1%NaCl-Salt	1.56
PEO400000 g/mol 5%conc. Without NaCl-Salt	0.016
PEO400000 g/mol 6%conc. With 1%NaCl-Salt	1.56
PEO900000 g/mol 2%conc. Without NaCl-Salt	0.016
PEO900000 g/mol 2%conc. With 1%NaCl-Salt	1.64
PEO900000 g/mol 3%conc. WithoutNaCl-Salt	0.016
PEO900000 g/mol 3%conc. With 1%NaCl-Salt	1.44

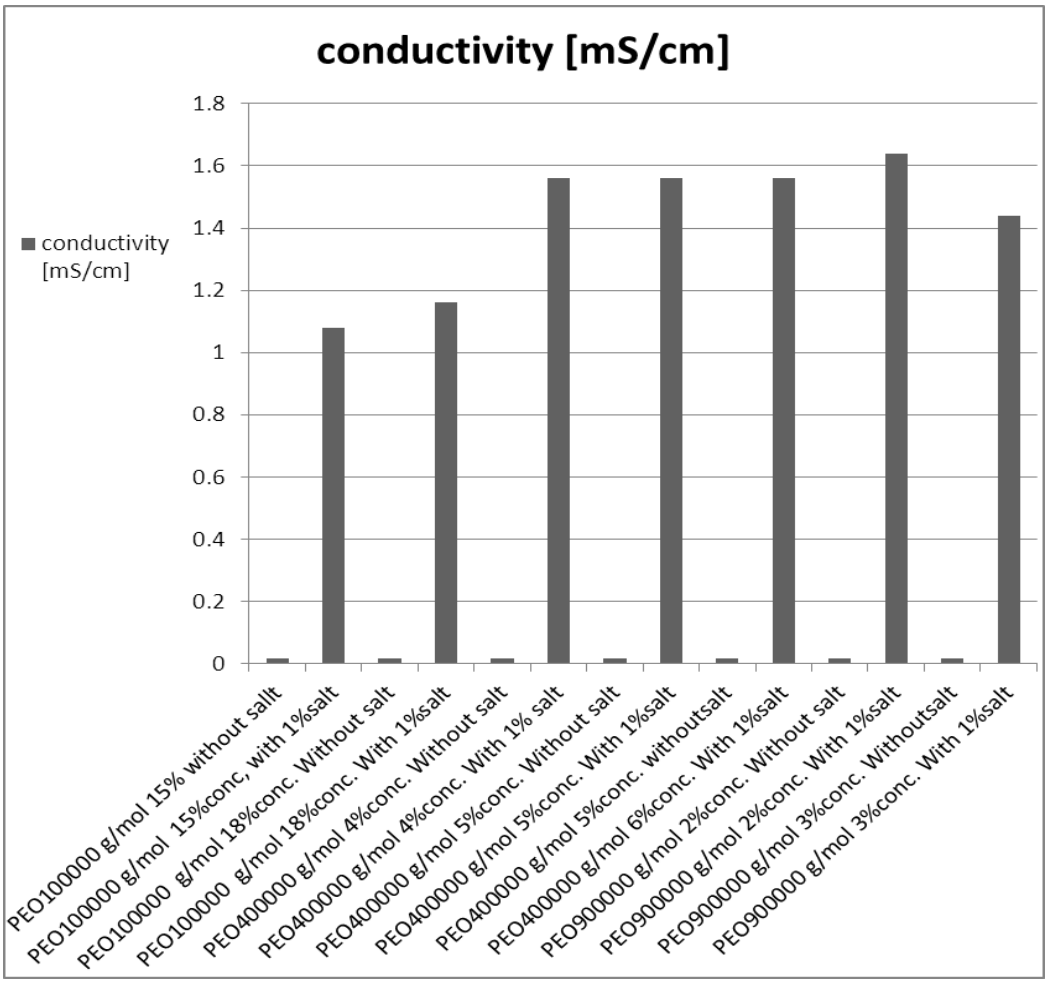


Figure 9 Polymer Conductivity graph

4.1.3 Polymer surface tension

Table 11 Polymer surface tension

polymer solutionat 25^0C	Surface Tension [mN/min] at20°c
PEO 100,000g/mol 15%conc 0%NaCl-Salt	62
PEO 100,000g/mol 15%conc 1%NaCl-Salt	61.3
PEO 100,000g/mol 18%conc 0%NaCl-Salt	62
PEO 100,000g/mol 18%conc 1%NaCl-Salt	61
PEO 400,000g/mol 4%conc 0%NaCl-Salt	61.3
PEO 400,000g/mol 4%conc 1%NaCl-Salt	61.5
PEO 400,000g/mol 5%conc 0%NaCl-Salt	61.1
PEO 400,000g/mol 5%conc 1%NaCl-Salt	60.6
PEO 400,000g/mol 6%conc 0%NaCl-Salt	69.3
PEO 400,000g/mol 6%conc 1%NaCl-Salt	66.5
PEO 900,000g/mol 2%conc 0%NaCl-Salt	63.4
PEO 900,000g/mol 2%conc 1%NaCl-Salt	63
PEO 900,000g/mol 3%conc 0%NaCl-Salt	64.7
PEO 900,000g/mol 3%conc 1%NaCl-Salt	63

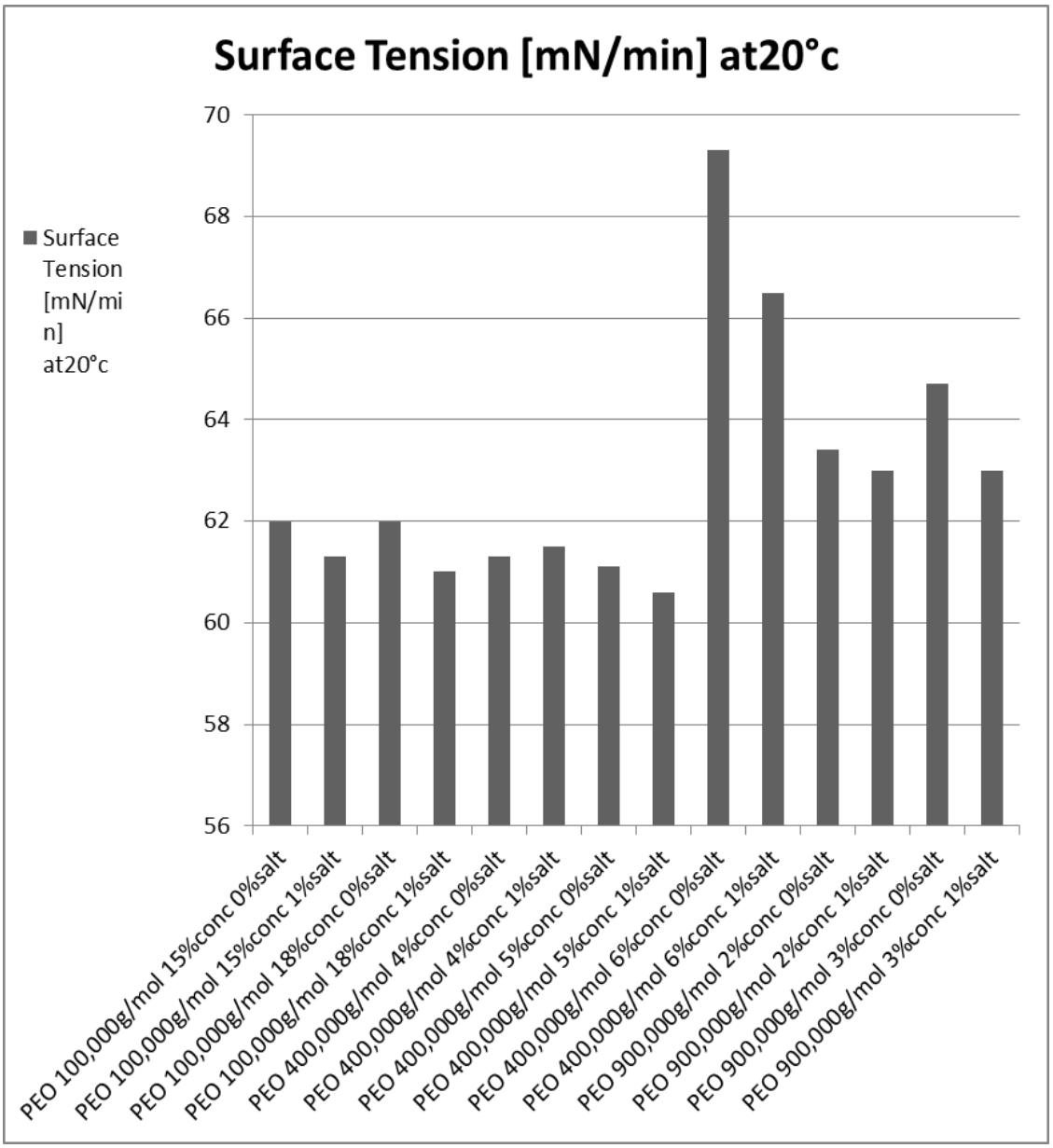


Figure 10Polymer Surface Tension

4.2 Needle spinning

Table 12 Needle Spinning observation

1	PEO 900,000 WITH 2%CONCENTRATION Nano fibers started producing from voltage of 15 kv and distance of ground plate 16 cm Ideal :25 kv and distance of plate 18 -24 cm
2	PEO 900,000 WITH 3% CONCENTRATION Nano fibers started producing from voltage of 15 kv and distance of ground plate 16 cm Ideal :25 kv and distance of plate 18 -24 cm
3	PEO 400,000 WITH 4% CONCENTRATION Nano fibers started producing from voltage of 15 kv and distance of ground plate 16 cm Ideal :25 kv and distance of plate 18 -24 cm
4	PEO 400,000 WITH 5% CONCENTRATION Nano fibers started producing from voltage of 15 kv and distance of ground plate 16 cm Ideal :25 kv and distance of plate 18 -24 cm
5	PEO 400,000 WITH 6% CONCENTRATION Nano fibers started producing from voltage of 15 kv and distance of ground plate 16 cm Ideal :25 kv and distance of plate 18 -24 cm
6	PEO 100,000 WITH 6% CONCENTRATION No Nano fibers produced
7	PEO 100,000 WITH 12% CONCENTRATION No Nano fibers produced
8	PEO 100,000 WITH 12% CONCENTRATION+8ml NaCl-Salt solution No Nano fibers produced
9	PEO 100,000 WITH 12% CONCENTRATION+16 ml NaCl-Salt solution No Nano fibers produced
10	PEO 100,000 WITH 18% CONCENTRATION +16 ml NaCl-Salt solution electro spraying from voltage of 20 kv and distance of ground plate 16 cm

4.3 Needle-less electrospinning

4.3.1 Roller spinning throughput

Table 13 Roller spinning throughput

polymer solutionat 25^{0}C	Throughput [g/m/min]
PEO 100,000g/mol 15%conc 0%NaCl-Salt	0
PEO 100,000g/mol 15%conc 1%NaCl-Salt	0
PEO 100,000g/mol 18%conc 0%NaCl-Salt	0
PEO 100,000g/mol 18%conc 1%NaCl-Salt	0
PEO 400,000g/mol 4%conc 0%NaCl-Salt	12.7
PEO 400,000g/mol 4%conc 1%NaCl-Salt	2.0
PEO 400,000g/mol 5%conc 0%NaCl-Salt	20.4
PEO 400,000g/mol 5%conc 1%NaCl-Salt	2.5
PEO 400,000g/mol 6%conc 0%NaCl-Salt	36.5
PEO 400,000g/mol 6%conc 1%NaCl-Salt	2.7
PEO 900,000g/mol 2%conc 0%NaCl-Salt	6.4
PEO 900,000g/mol 2%conc 1%NaCl-Salt	1.5
PEO 900,000g/mol 3%conc 0%NaCl-Salt	13.4
PEO 900,000g/mol 3%conc 1%NaCl-Salt	4.0

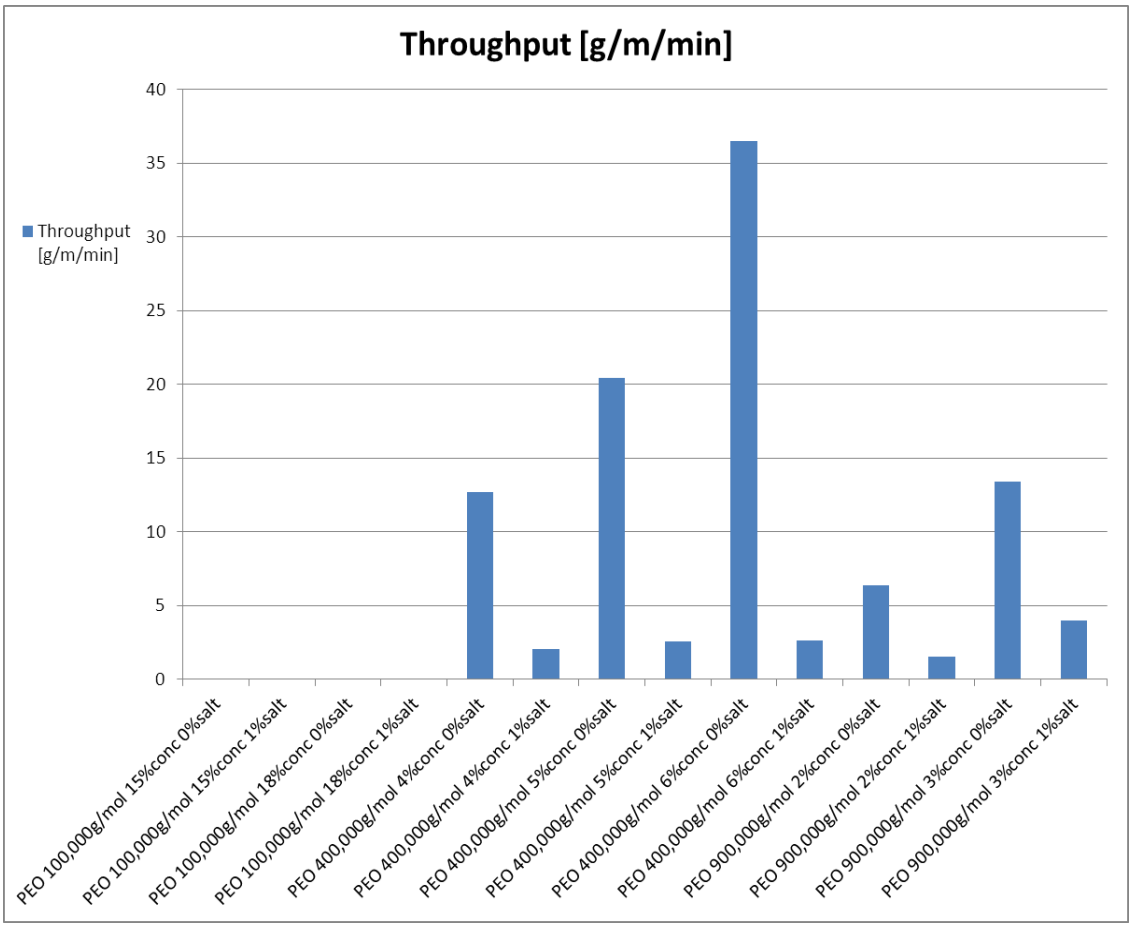


Figure 11Roller spinning throughput graph

4.3.2 Throughput PEO Mw400,000 with 6%concentration

Table 14 Throughput PEO Mw400,000 with 6%concentration

polymer solutionat 24°C 25%RH	Throughput [g/m/min]	NaCl-Salt (%)
PEO 400,000g/mol 6%conc 0%NaCl-Salt	31	0
PEO 400,000g/mol 6%conc 0.1%NaCl-Salt	12	0.1
PEO 400,000g/mol 6%conc 0.3%NaCl-Salt	5.2	0.3
PEO 400,000g/mol 6%conc 0.5%NaCl-Salt	4.6	0.5
PEO 400,000g/mol 6%conc 1%NaCl-Salt	2.5	1
PEO 400,000g/mol 6%conc 1.5%NaCl-Salt	2.1	1.5
PEO 400,000g/mol 6%conc 2%NaCl-Salt	1.4	2

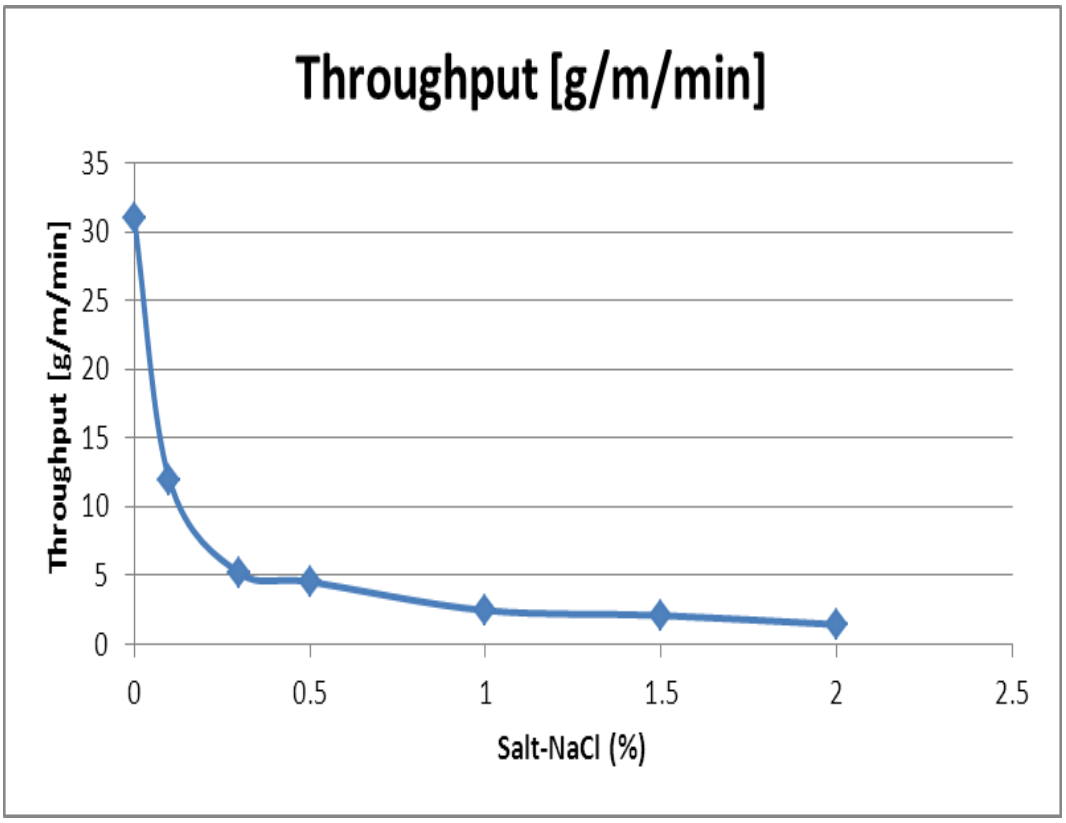


Figure 12 Throughput PEO Mw400,000 with 6%concentration graph

4.3.3 Fiber diameter [image analysis]

Table 15 Fiber diameter

	polymer	Average Diameter [nm]	Standard deviation
1	PEO 400,000g/mol 4%conc 1%salt	160	40
2	PEO 400,000g/mol 5%conc 1%salt	188	38
3	PEO 400,000g/mol 6%conc 1%salt	213	44
4	PEO 900,000g/mol 2%conc 0%salt	121	62
5	PEO 900,000g/mol 2%conc 1%salt	123	24
6	PEO 900,000g/mol 3%conc 0%salt	128	58
7	PEO 900,000g/mol 3%conc 1%salt	129	21

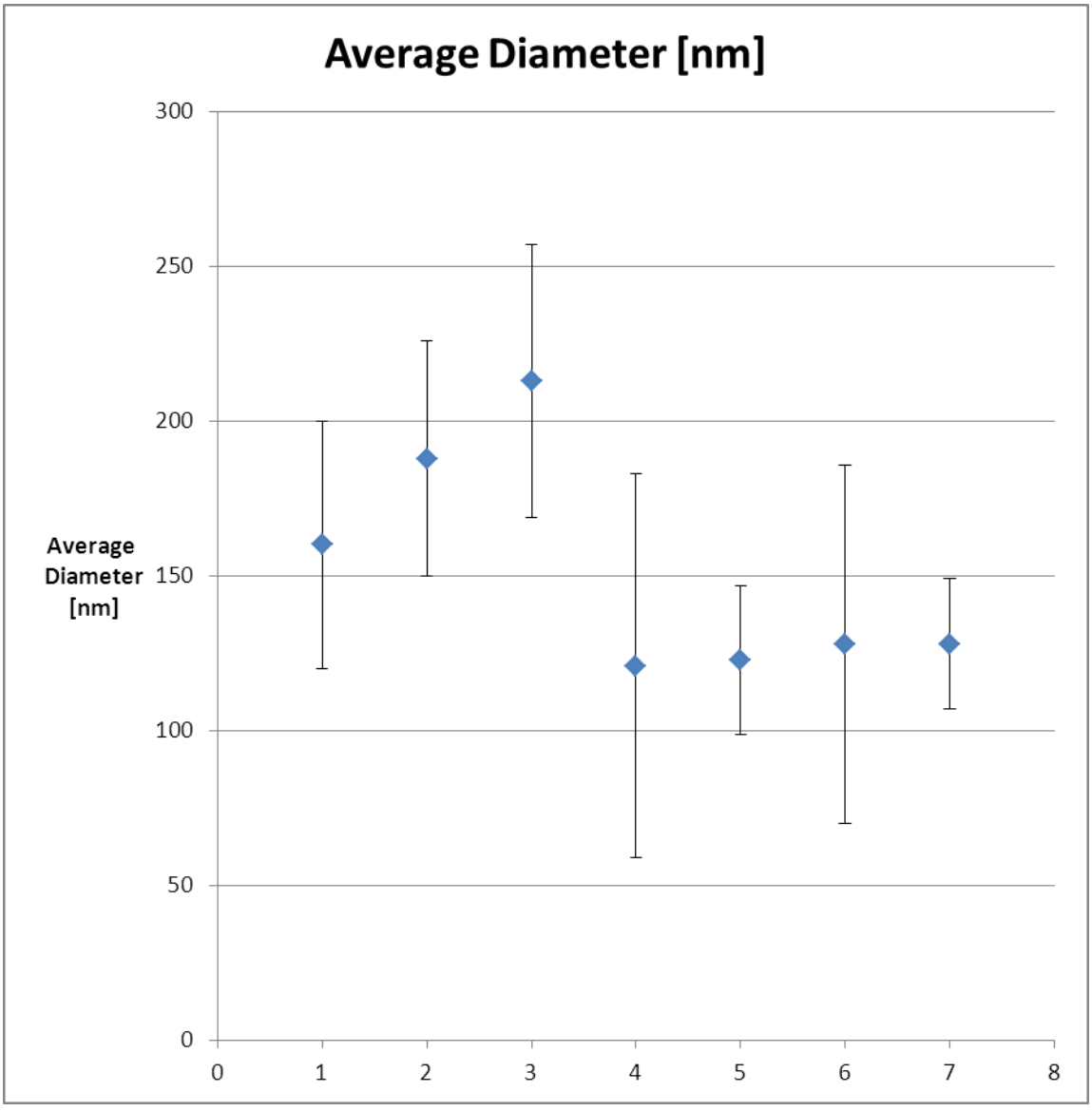


Figure 13 Average fiber diameter needle-less electrospinning

4.3.4 Comparison of Viscosity and throughput

Table 16 Comparison of Viscosity and throughput

Polymer	Throughput[g/m/min]	Zero shear rate Viscosity [Pa.s]
PEO 900,000g/mol 2%conc 1%salt	1.54	0.12
PEO 900,000g/mol 2.5%conc 1%salt	3.01	0.27
PEO 900,000g/mol 3%conc 1%salt	3.99	0.4
PEO 900,000g/mol 3.5%conc 1%salt	4.45	0.53
PEO 400,000g/mol 4%conc 1%salt	2.04	0.4
PEO 400,000g/mol 4.5%conc 1%salt	2.35	0.51
PEO 400,000g/mol 5%conc 1%salt	2.53	0.65
PEO 400,000g/mol 5.5%conc 1%salt	2.59	1.02
PEO 400,000g/mol 6%conc 1%salt	2.65	1.4

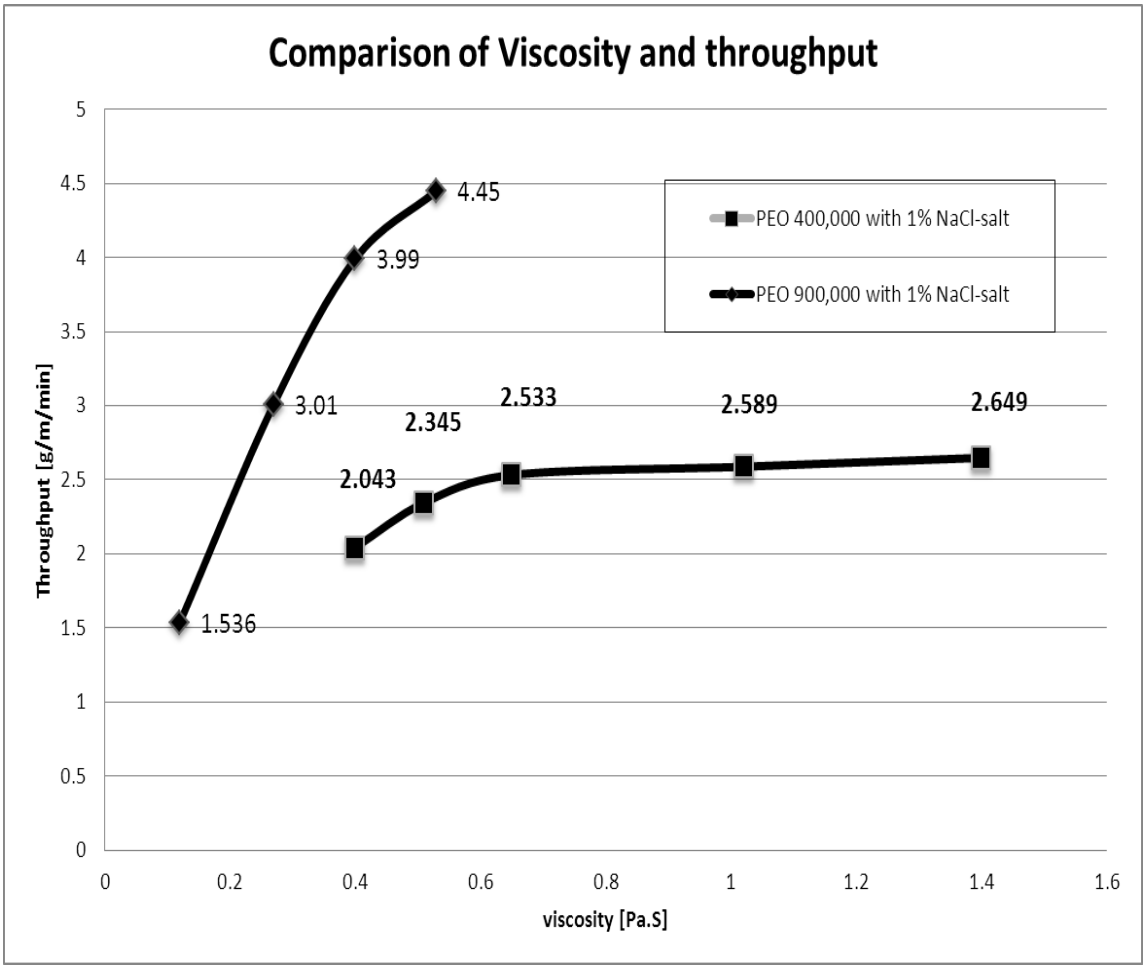


Figure 14graph for Comparison of Viscosity and throughput

4.3.5 Comparison of concentration and throughput

Table 17 Comparison of concentration and throughput

Polymer solution	Throughput[g/m/min]	Concentration [%]
PEO 900,000g/mol 1%salt	1.54	2
PEO 900,000g/mol 1%salt	3.01	2.5
PEO 900,000g/mol 1%salt	3.99	3
PEO 900,000g/mol 1%salt	4.45	3.5
PEO 400,000g/mol 1%salt	2.04	4
PEO 400,000g/mol 1%salt	2.35	4.5
PEO 400,000g/mol 1%salt	2.53	5
PEO 400,000g/mol 1%salt	2.59	5.5
PEO 400,000g/mol 1%salt	2.65	6

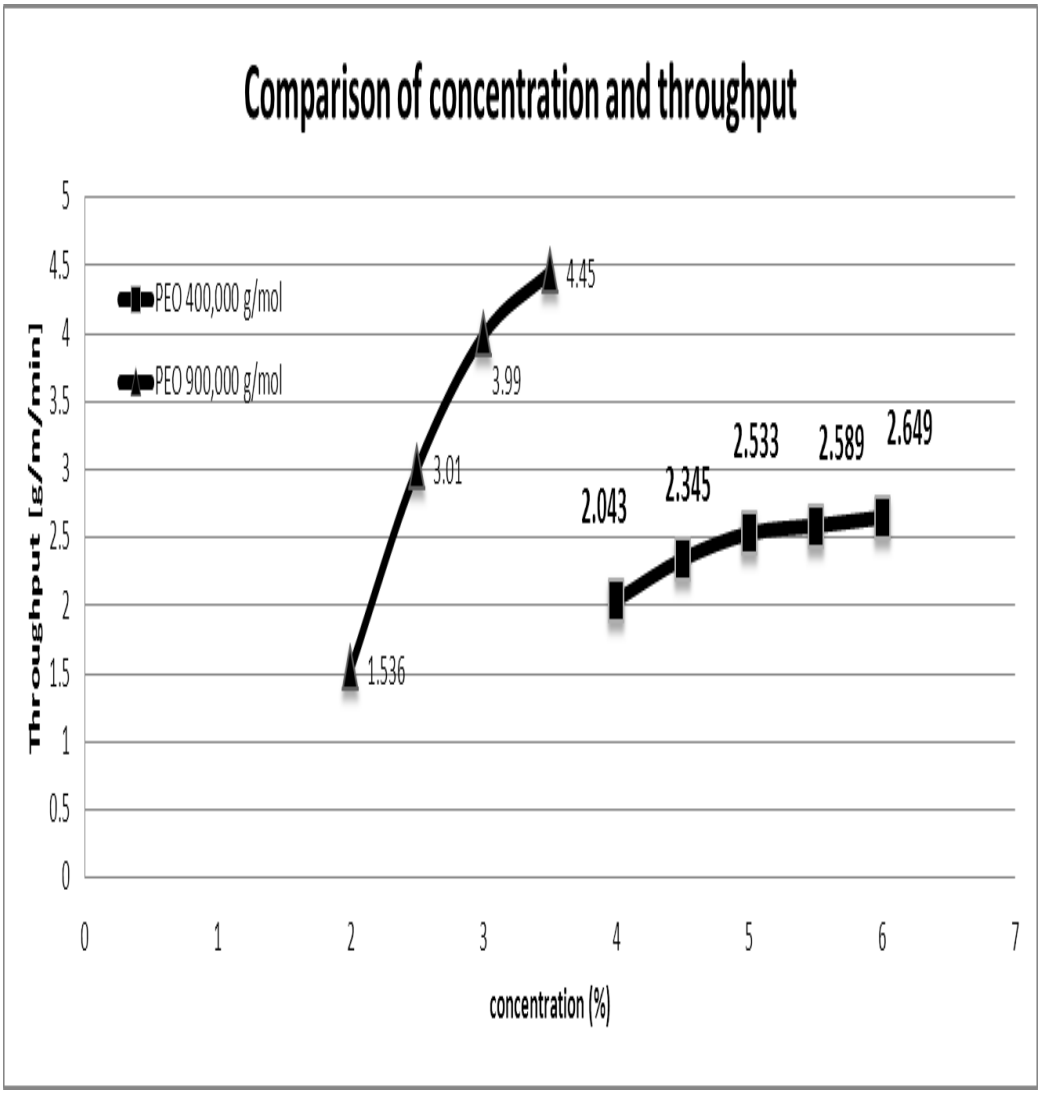


Figure 15 Graph for comparison of concentration and throughput

4.3.6 NaCl-salt effect on surface tension of polymer solution

Table 18 NaCl-salt percentage and surface tension

polymer solutionat 24°C 25%RH	Throughput [g/m/min]	NaCl-Salt (%)	surface tension (mN/m)
PEO 400,000g/mol 6%conc 0%NaCl-Salt	31	0	69.5
PEO 400,000g/mol 6%conc 0.1%NaCl-Salt	12	0.1	69.7
PEO 400,000g/mol 6%conc 0.3%NaCl-Salt	5.2	0.3	69.4
PEO 400,000g/mol 6%conc 0.5%NaCl-Salt	4.6	0.5	69.3
PEO 400,000g/mol 6%conc 1%NaCl-Salt	2.5	1	68.7
PEO 400,000g/mol 6%conc 1.5%NaCl-Salt	2.1	1.5	68.9
PEO 400,000g/mol 6%conc 2%NaCl-Salt	1.4	2	69.2

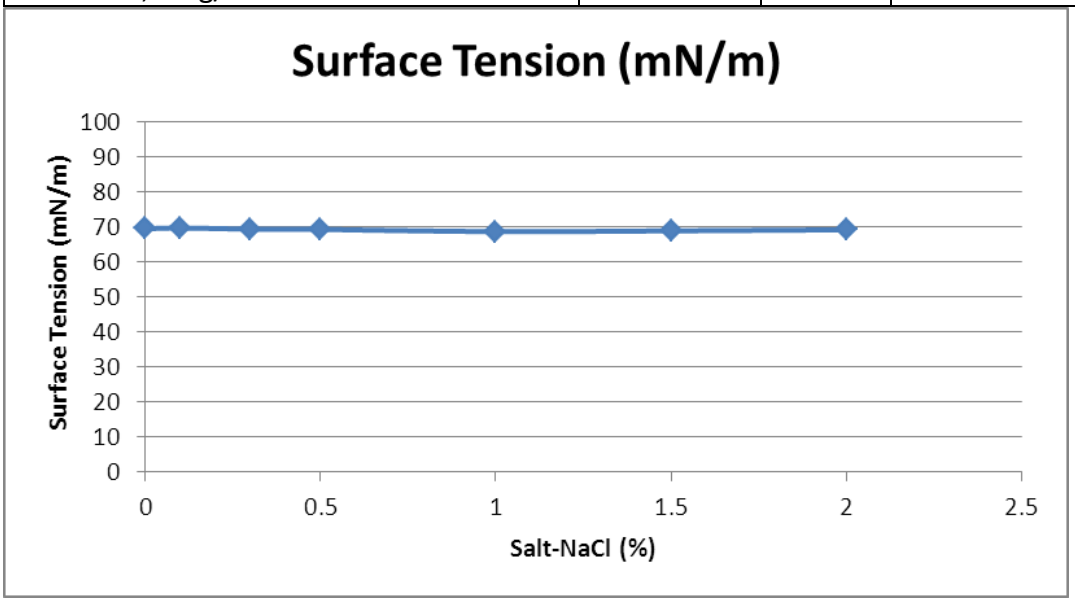


Figure 16 Graph NaCl-salt effect on surface tension

4.3.7 NaCl-salt effect on conductivity of polymer solution

Table 19 NaCl-salt and conductivity

polymer solutionat 24°C 25%RH	Throughput [g/m/min]	NaCl-Salt (%)	surface tension (mN/m)	Conductivity mS/cm)
PEO 400,000g/mol 6%conc	31	0	69.5	0.016
PEO 400,000g/mol 6%conc	12	0.1	69.7	0.13
PEO 400,000g/mol 6%conc	5.2	0.3	69.4	0.45
PEO 400,000g/mol 6%conc	4.6	0.5	69.3	0.98
PEO 400,000g/mol 6%conc	2.5	1	68.7	1.56
PEO 400,000g/mol 6%conc	2.1	1.5	68.9	2.45
PEO 400,000g/mol 6%conc	1.4	2	69.2	4.6

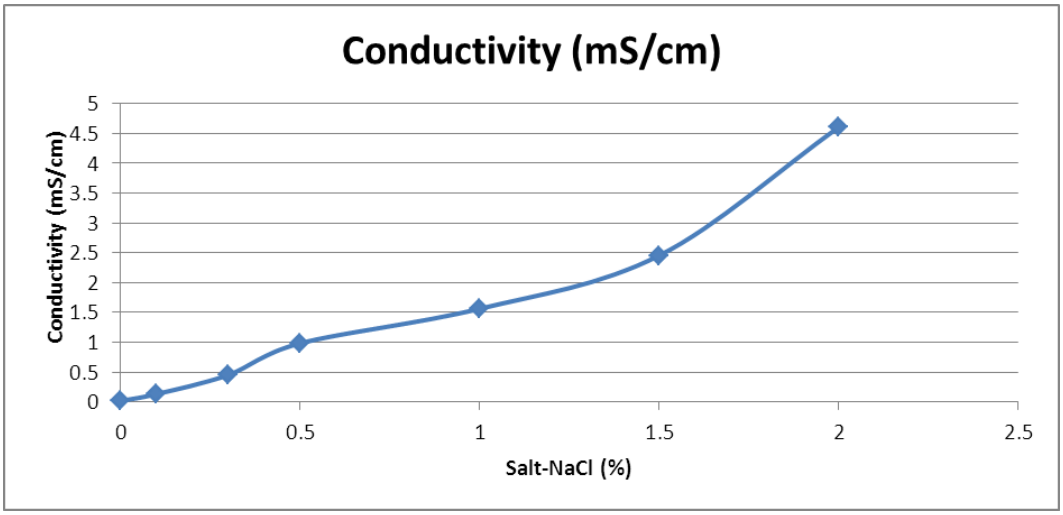


Figure 17Graph NaCl-salt effect on conductivity

4.3.8 NaCl-salt effect on viscosity of polymer solution

Table 20 NaCl-salt effect on viscosity

polymer solutionat 24°C 25%RH	NaCl-Salt (%)	Zero shear Viscosity (Pa.s)
PEO 400,000g/mol 6%conc	0	1.23
PEO 400,000g/mol 6%conc	0.1	1.25
PEO 400,000g/mol 6%conc	0.3	1.3
PEO 400,000g/mol 6%conc	0.5	1.35
PEO 400,000g/mol 6%conc	1	1.4
PEO 400,000g/mol 6%conc	1.5	1.45
PEO 400,000g/mol 6%conc	2	1.5

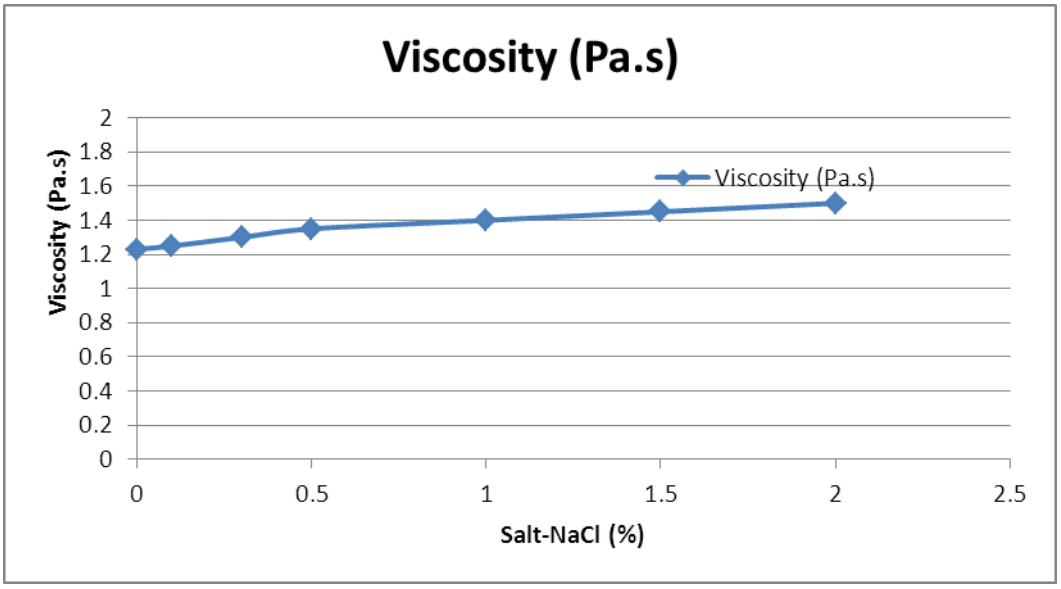


Figure 18 Graph of naCl-salt effect on Zero shear viscosity

4.4 Comparison Needle and Needle-less Electrospinning

4.4.1 NaCl-salt effect on Non-fibrous area in needle electrospinning

Table 21NaCl-salt effect on NFA in needle electrospinning

polymer solutionat 24^{0}C 25%RH	Throughput [g/m/min]	NFA(%) Needleless spinning	NFA(%)Needle spinning
PEO 400,000g/mol 6%conc 0%NaCl-Salt	31	11.4	2.6
PEO 400,000g/mol 6%conc 0.1%NaCl-Salt	12	2.4	0
PEO 400,000g/mol 6%conc 0.3%NaCl-Salt	5.2	0.98	0
PEO 400,000g/mol 6%conc 0.5%NaCl-Salt	4.6	0.45	0
PEO 400,000g/mol 6%conc 1%NaCl-Salt	2.5	0.11	0
PEO 400,000g/mol 6%conc 1.5%NaCl-Salt	2.1	0.09	0
PEO 400,000g/mol 6%conc 2%NaCl-Salt	1.4	0.08	0

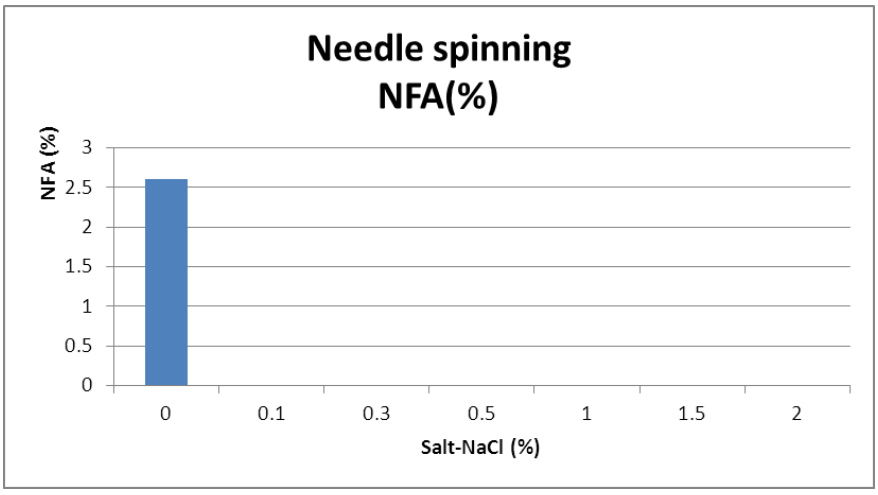


Figure 19Graph for Nacl-salt effect on NFA in needle electrospinning

4.4.2 NaCl-salt effect on Non-fiborous area in needle-less electrospinning

Table 22 Nacl-salt and NFA in needle-less electrospinning

polymer solutionat 24^{0}C 25%RH	Throughput [g/m/min]	NaCl-Salt (%)	NFA(%) Needleless spinning
PEO 400,000g/mol 6%conc	31	0	11.4
PEO 400,000g/mol 6%conc	12	0.1	2.4
PEO 400,000g/mol 6%conc	5.2	0.3	0.98
PEO 400,000g/mol 6%conc	4.6	0.5	0.45
PEO 400,000g/mol 6%conc	2.5	1	0.11
PEO 400,000g/mol 6%conc	2.1	1.5	0.09
PEO 400,000g/mol 6%conc	1.4	2	0.08

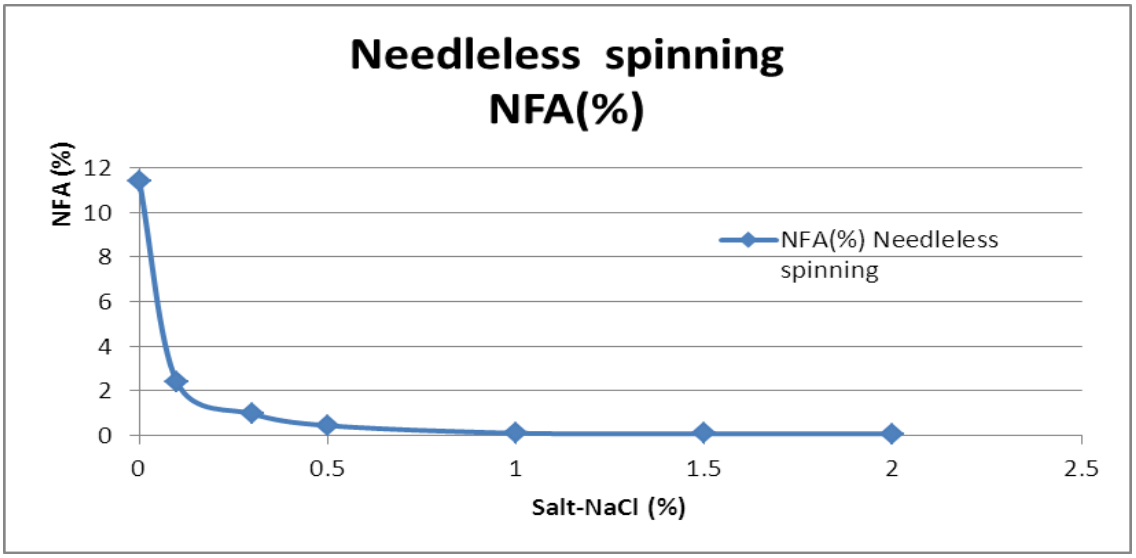


Figure 20Graph of NaCl-salt and NFA in needle-less electrospinning

4.4.3 Comparison Fiber diameter for needle and needle-less electrospinning

Table 23 NaCl-salt effect on fiber diameter in needle-less electrospinning

polymer solutionat 24°C 25%RH	Fiber Diameter(nm)	STD.DEV	NaCl-Salt (%)
PEO 400,000g/mol 6%conc 0%NaCl-Salt	181	80	0
PEO 400,000g/mol 6%conc 0.1%NaCl-Salt	181	45	0.1
PEO 400,000g/mol 6%conc 0.3%NaCl-Salt	182	38	0.3
PEO 400,000g/mol 6%conc 0.5%NaCl-Salt	183	42	0.5
PEO 400,000g/mol 6%conc 1%NaCl-Salt	196	37	1
PEO 400,000g/mol 6%conc 1.5%NaCl-Salt	206	39	1.5
PEO 400,000g/mol 6%conc 2%NaCl-Salt	210	24	2

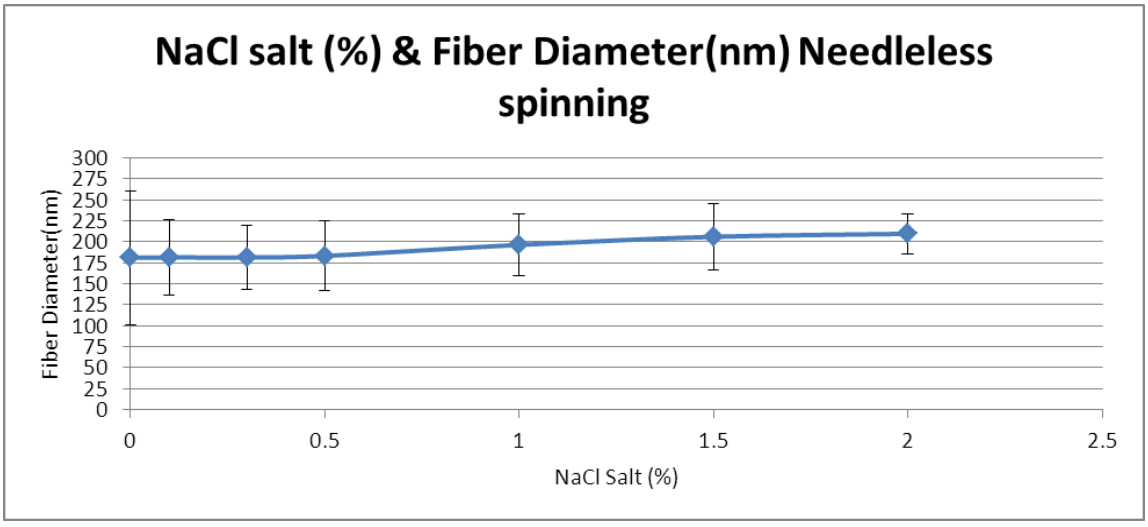


Figure 21Graph of NaCl-salt effect on fiber diameter in needle-less electrospinning

Table 24 NaCl-salt effect on fiber diameter in needle electrospinning

polymer solutionat 24^{0}C 25%RH	Fiber Diameter(nm)	STD.DEV	NaCl-Salt (%)
PEO 400,000g/mol 6%conc	123	60	0
PEO 400,000g/mol 6%conc	125	24	0.1
PEO 400,000g/mol 6%conc	128	18	0.3
PEO 400,000g/mol 6%conc	129	17	0.5
PEO 400,000g/mol 6%conc	130	25	1
PEO 400,000g/mol 6%conc	131	22	1.5
PEO 400,000g/mol 6%conc	132	30	2

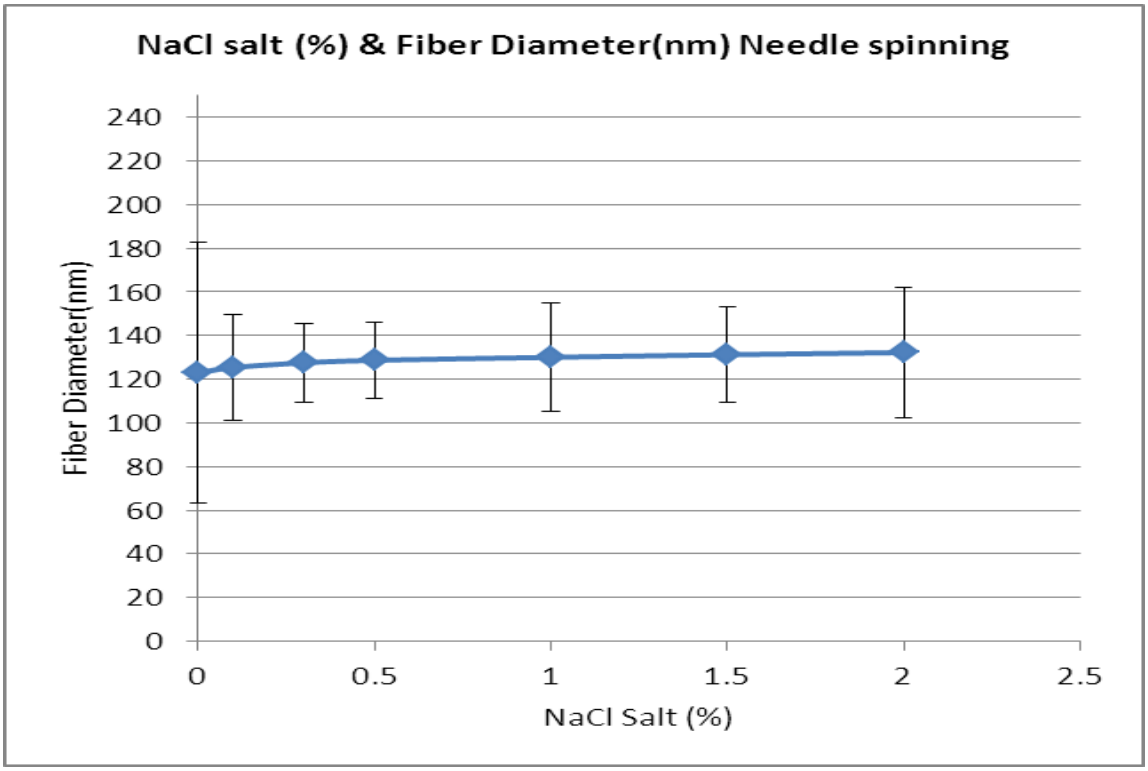


Figure 22 Graph of NaCl-salt effect on fiber diameter in needle electrospinning

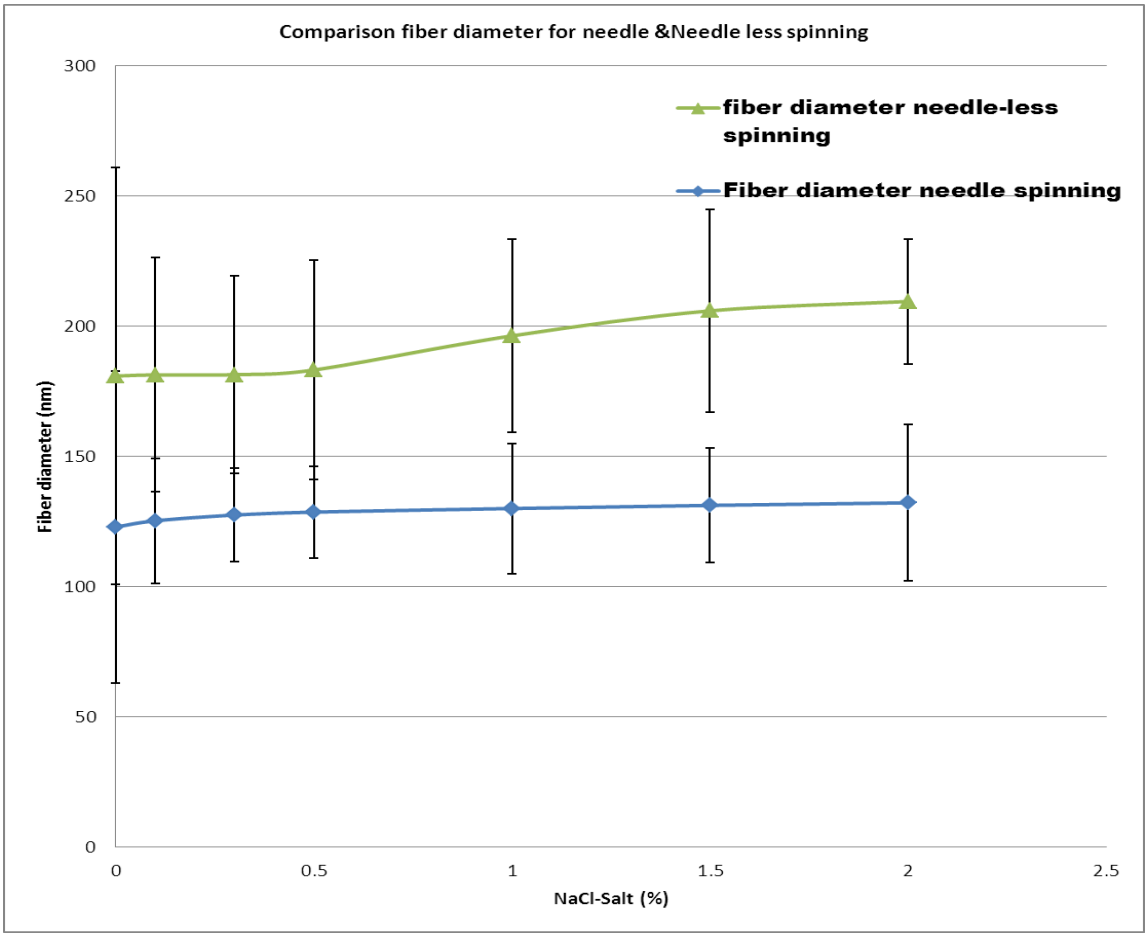


Figure 23 Graph for comparison of fiber diameter of needle and needle-less electrospinning

4.4.4 FiberDiameter distribution

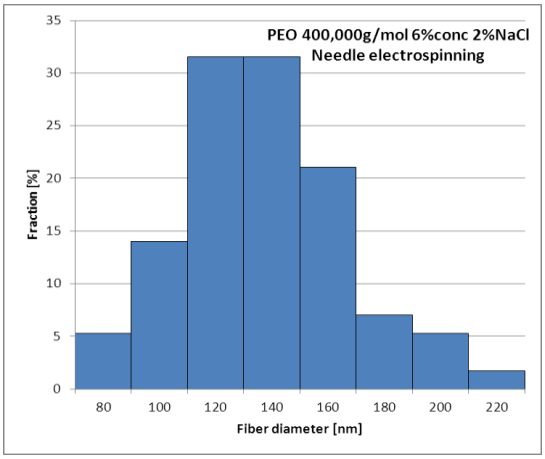


Figure 24 Fiber diameter distribution PEO 400,000 g/mol 6%conc.2%NaCl-salt ,needle spinning

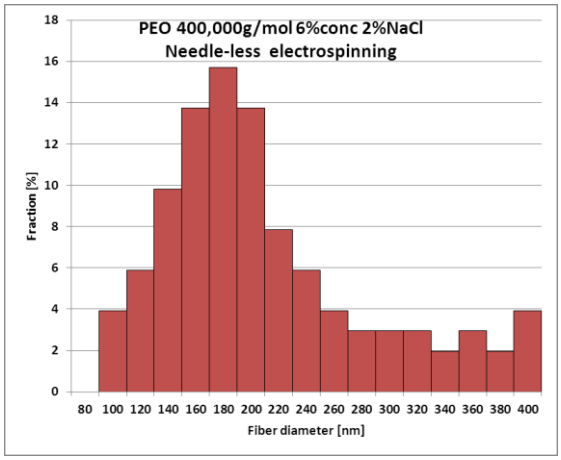


Figure27Fiberdiameter distribution PEO400,000 g/mol 6%conc.2%NaCl-salt ,needle-less spinning

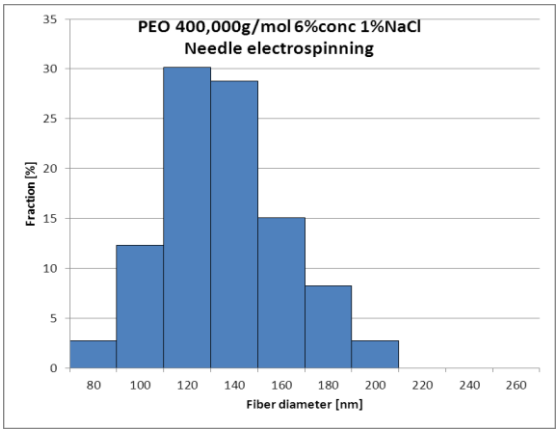


Figure 25 Fiber diameter distribution PEO400,000 g/mol 6%conc.1%NaCl-salt ,needle spinning

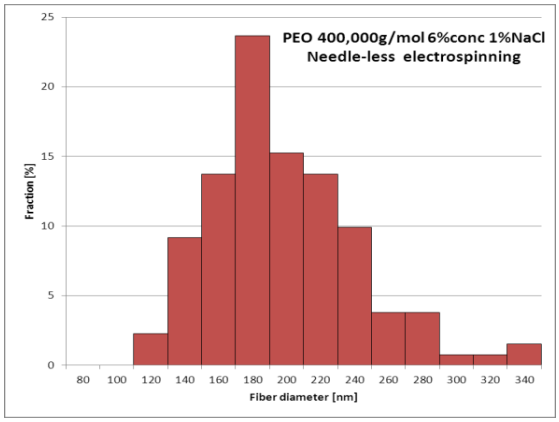


Figure 28 Fiber diameter distribution PEO400,000 g/mol 6%conc.1%NaCl-salt ,needle-less spinning

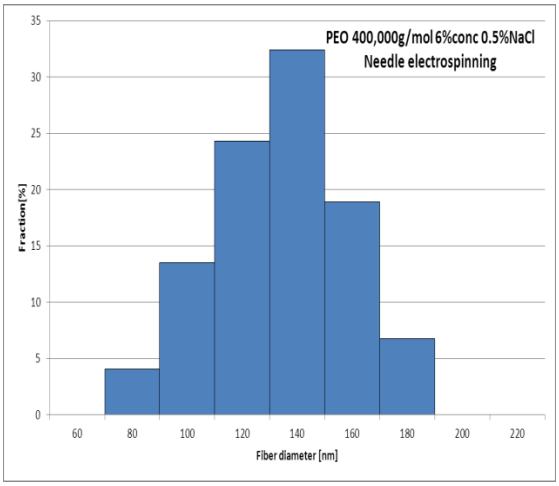


Figure 26 Fiber diameter distribution PEO400,000 g/mol 6%conc.0.5%NaCl-salt ,needle spinning

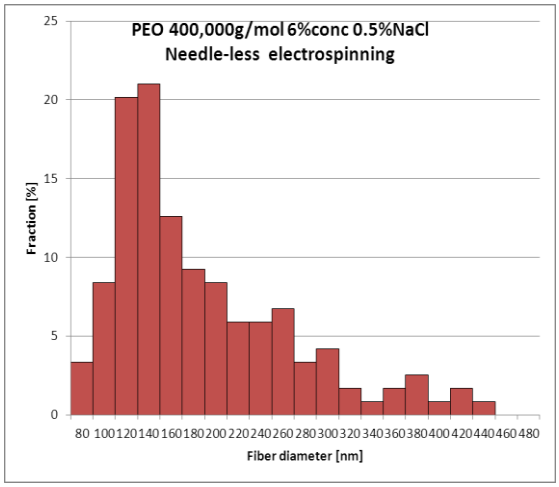


Figure 29 Fiber diameter distribution PEO400,000 g/mol 6%conc.0.5%NaCl-salt ,needle-less spinning

4.5 Electron Microscope Images

4.5.1 Needle Electrospinning Images

PEO 100,000 g/mol with 18%Nacl-salt electron microscope image

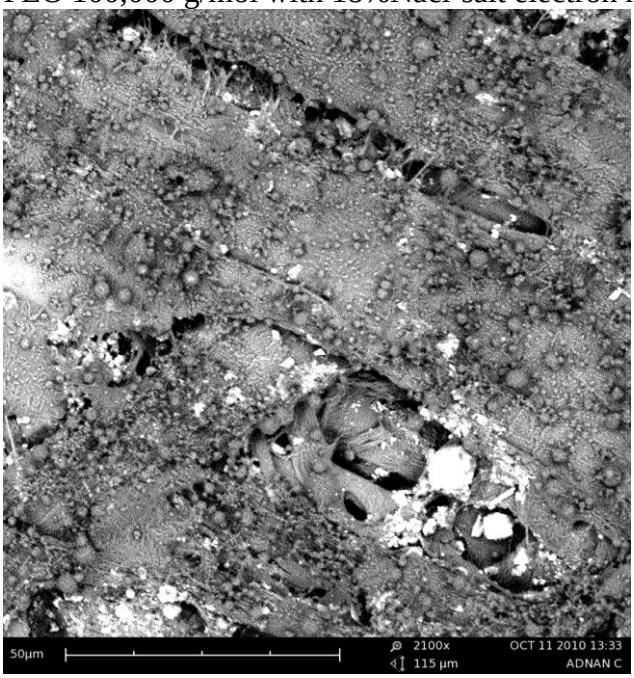


Figure 30 PEO100,000 g/mol with 18%Nacl-salt electro microscope image

PEO 400,000 g/mol 6%conc.0%NaCl-salt needle electrsospinning

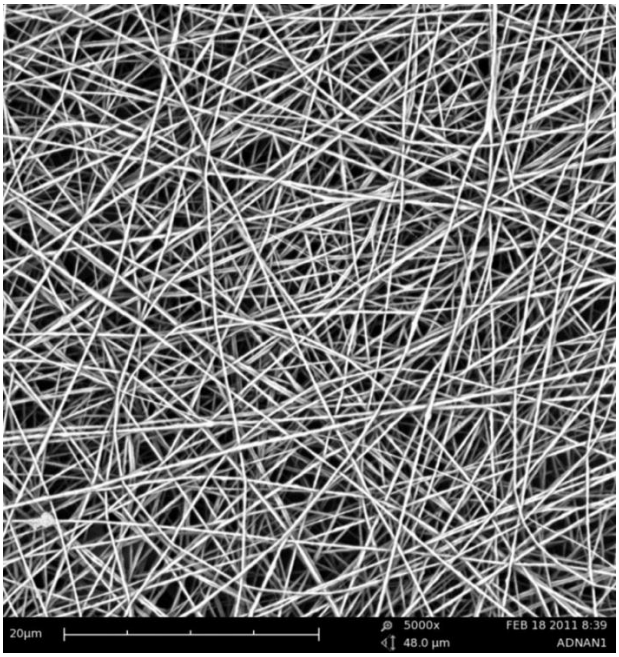


Figure 31 PEO 400,000 g/mol 6%conc.0%NaCl-salt needle electrsospinning

PEO 400,000 g/mol 6%conc.0.5%NaCl-salt needle electrsospinning

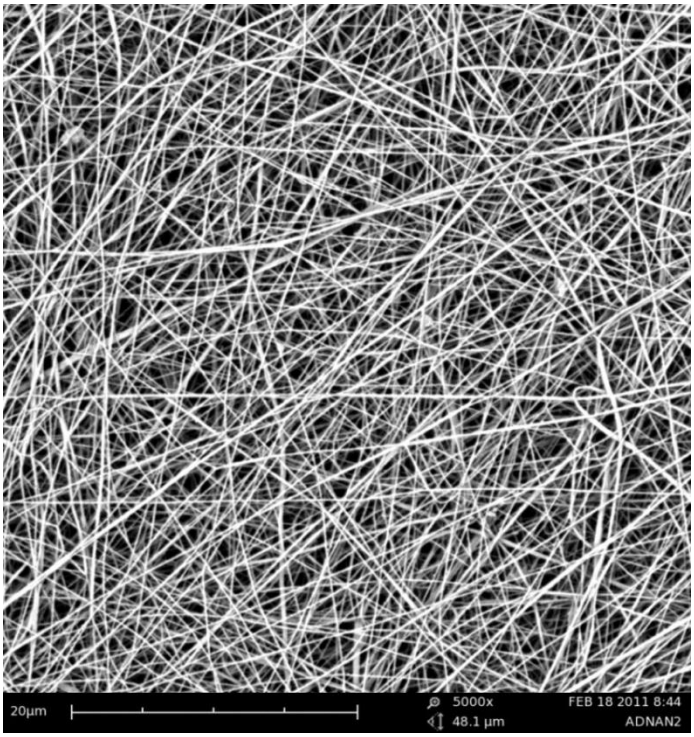


Figure 32 PEO 400,000 g/mol 6%conc.0.5%NaCl-salt needle electrsospinning

PEO 400,000 g/mol 6%conc. 1 %NaCl-salt needle electrsospinning

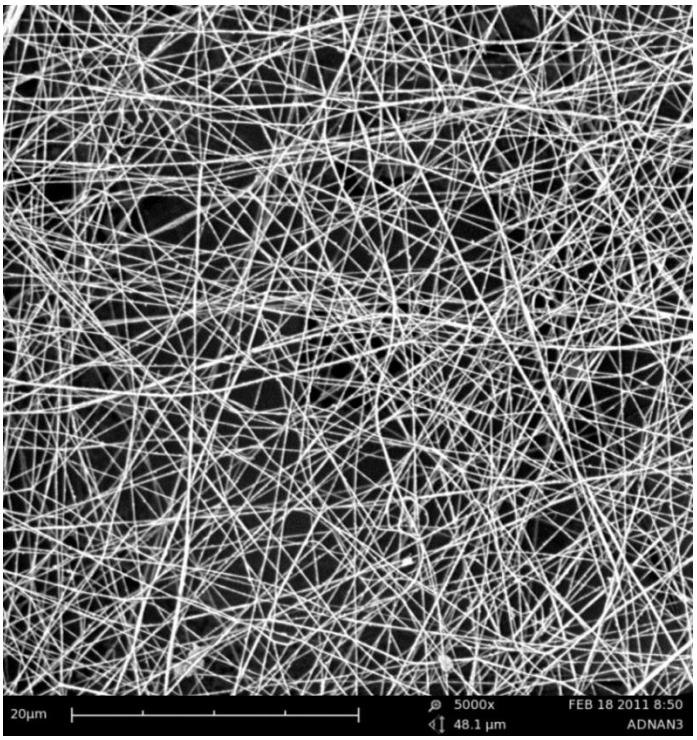


Figure 33 PEO 400,000 g/mol 6%conc. 1 %NaCl-salt needle electrsospinning

PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle electrsospinning

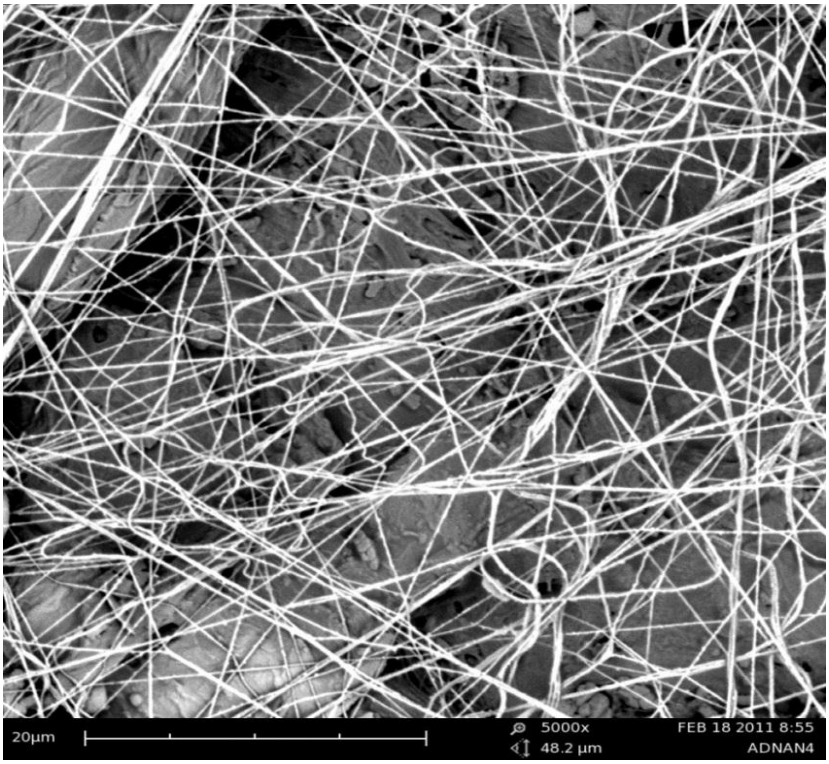


Figure 34 PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle electrsospinning

4.5.2 Needle-less electrospinning Images

PEO 400,000 g/mol 6%conc. 0%NaCl-salt needle-less electrsospinning

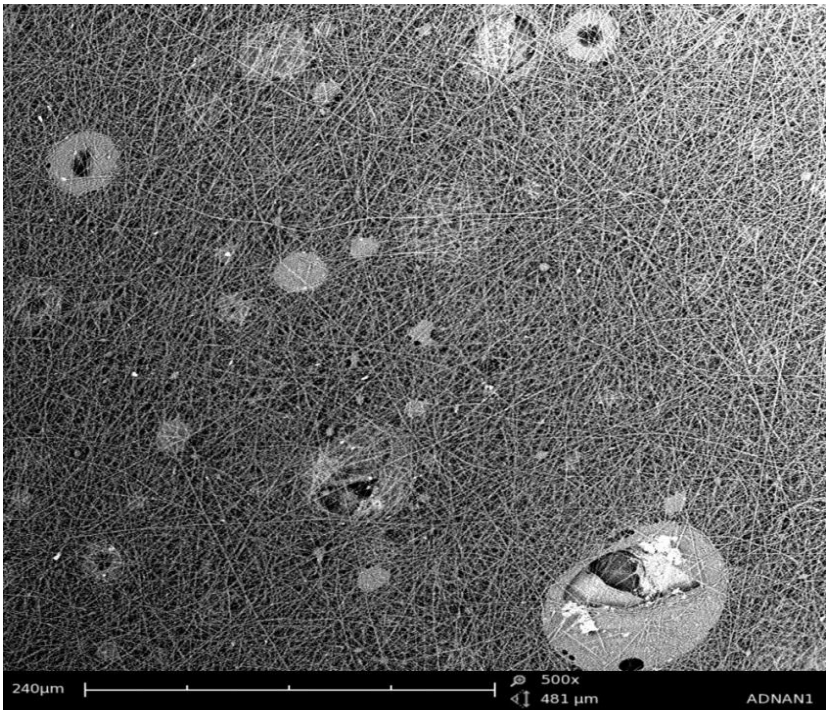


Figure 35 PEO 400,000 g/mol 6%conc. 0%NaCl-salt needle-less electrsospinning

PEO 400,000 g/mol 6%conc. 0.5 %NaCl-salt needle-less electrsospinning

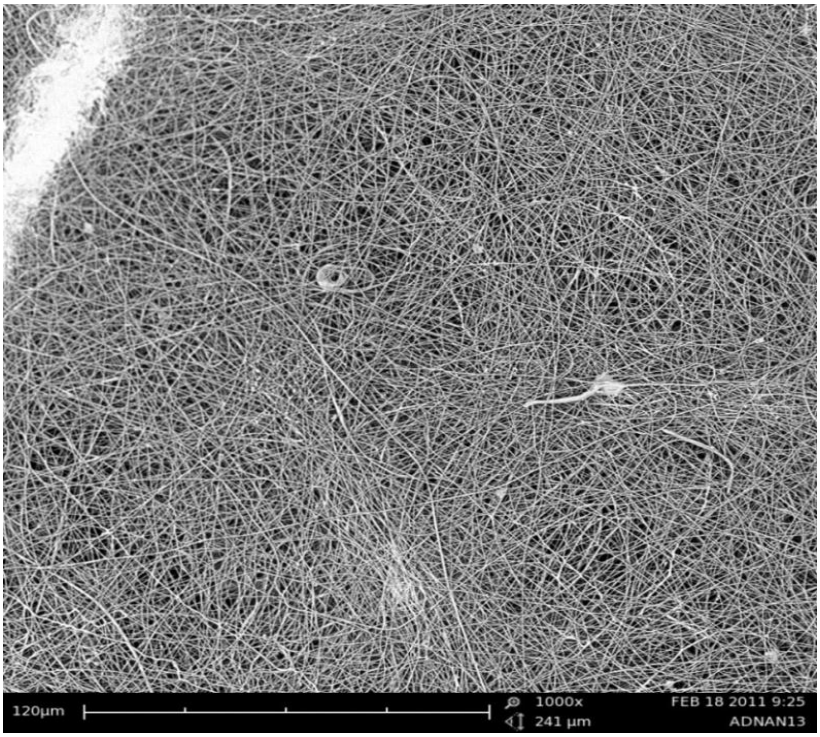


Figure 36 PEO 400,000 g/mol 6%conc. 0.5 %NaCl-salt needle-less electrsospinning

PEO 400,000 g/mol 6%conc. 1 %NaCl-salt needle-less electrsospinning

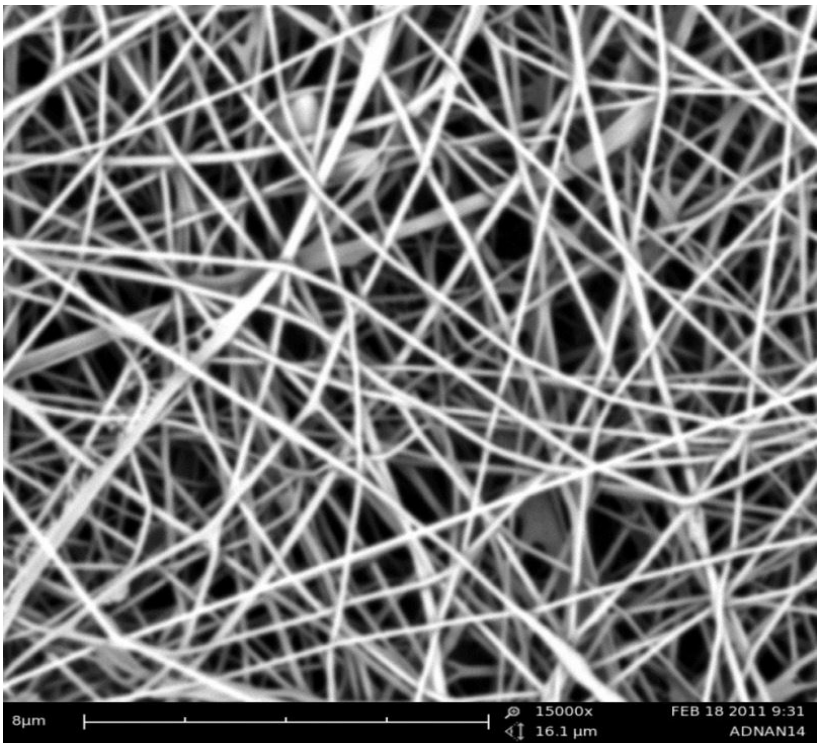


Figure 37 PEO 400,000 g/mol 6%conc. 1 %NaCl-salt needle-less electrsospinning

PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle-less electrsospinning

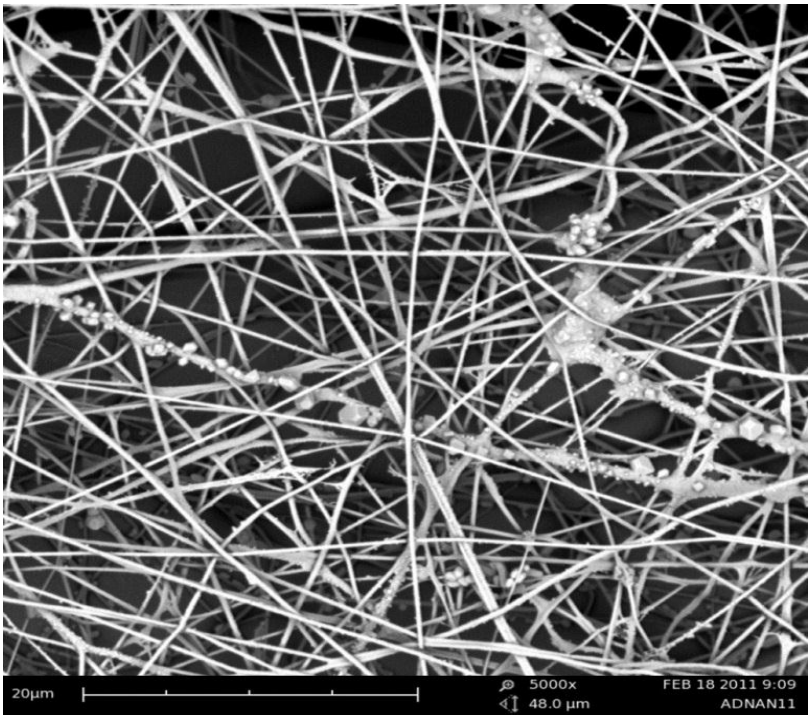


Figure 38 PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle-less electrsospinning

4.5.2.1 NaCl-Salt crystals

PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle-less electrsospinning

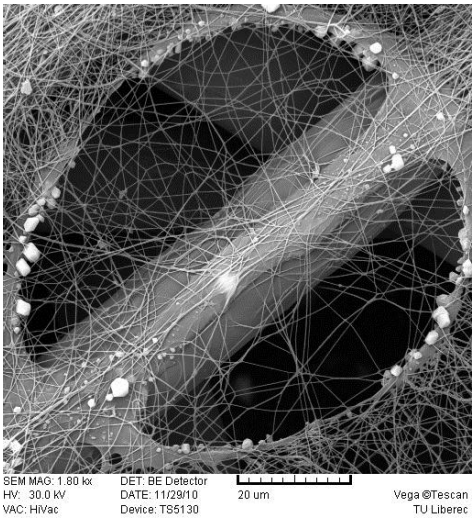


Figure 40 PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle-less electrsospinning showing NaCl-salt crystals

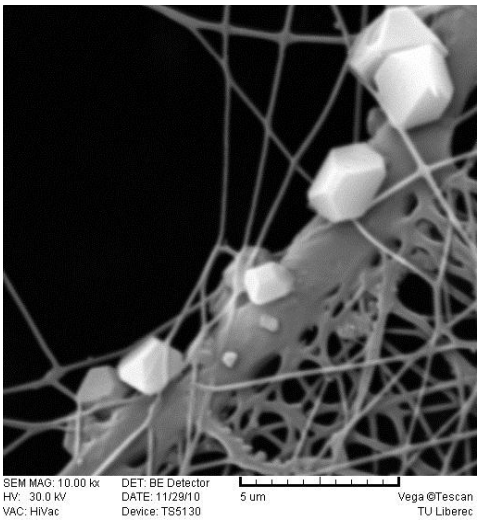


Figure 39 PEO 400,000 g/mol 6%conc. 2 %NaCl-salt needle-less electrsospinning showing NaCl-salt crystals

5 Discussions

Based on the results presented in chapter 5, this chapter will describe in details the relationships between the Needle and Needle-less electrospinning.Different parameters will be used to explain the relationships regarding throughput,Non-fiborous area,Fiber diameter, viscosity, concentration, surface tension ,Fiber diameter distribution ,NaCl-salt effect and fiber quality.

5.1 Effects of polymer molecular weight and its solution concentration

5.1.1 On spinning ability of PEO polymer solutions

The results illustrated in above results shows that the differences in electric conductivity and surface tension of studied solutions are not significant. Conditions of electrospinning were the same for all the materials. Therefore, we can assume that only molecular weight of polymers and concentrations of solutions are responsible for significant differences in spinnability, throughput and fiber quality.

There is a significant difference between a needle and surface (or roller) electrospinning process. In the hollow needle, the polymer solution is moved ahead by mechanical forces. Thus, it is transported to high field strength position where it has the best conditions for spinning process. When the spinning occurs, spinning jet is always supplied with fresh solution by mechanical forces. When leaving the needle, the solution is formed by electric field into droplets or fibers, depending on polymer properties. In the roller electrospinning, Taylor cones are created on the surface of polymer solution as described by Lukas at [50]. In the spinning process, the jet always must seek for food (supply of fresh material) from surrounding of Taylor cone. Otherwise the Taylor cone disappears in short time because of lack of fresh polymer solution. Certain level of the strength is necessary to enable the jet to suck in fresh solution. Strength of the jet depends on the level of intermolecular entanglements. The jet is simultaneously a tool for electrical forces to take polymer material from free surface of polymer solution. If the intermolecular entanglements and the jets are strong enough, the spinning process will continue. On the contrary, if the jets are weak, they break in a very short time, Taylor cones disappear and the spinning process stops.

Generally, there are two conditions for receiving a stable Taylor cone. First, the jet must be strong enough to stabilize Taylor cone by mechanical forces as it is pulled toward

collector electrode. As soon as the jet breaks, Taylor cone disappears. A droplet or non-fibrous particle may be created in this moment. Nevertheless, the spinning process does not continue. Thus, non-stable formation of solution typical for low molecular weight polymers and for electro-spraying in the needle process does not start spinning process on the roller.

The second condition for a stable Taylor cone is the ability of the solution to feed Taylor cones with fresh material from surroundings. This requires limited solution viscosity and suitable rheological behaviour. A stable Taylor cone is able to yield a jet during several seconds to tens of seconds. A stable Taylor cone also gives chance for surrounding area to create another Taylor cone. That is the reason why jets spread to almost all the surface in spinning area.

5.2 Effect of conductivity

By adding various concentration of sodium chloride, the surface tension and viscosity of PEO polymer solution do not change significantly. On the contrary, conductivity of the solution increases strongly with increasing concentration of sodium chloride . It means that sodium chloride does not affect the structure of PEO solutions. This slightly increases the friction coefficient between molecules inside solution. On the other hand, it brings a huge amount of ions into solution which causes conductivity of solution increase strongly.

Graphs in Fig16-Fig 20 show dependence of some parameters on conductivity. Values of spinning performance (throughput) strongly depend on conductivity of spinning solution or on concentration of sodium chloride, respectively. Under the same spinning conditions, the higher is conductivity the lower is throughput as illustrated in Fig.12.

5.3 Fiber Diamter

Fig 23 clearly shows that the fiber diameter of needle spinning is much less than that of needle-less spinning and the fiber diameter distribution shows that in needle-less spinning the fiber diameter is distributed with greater standard deviation, Fig 24-Fig 29. Because in needle-less spinning there are more chances of material to be pulled apart from the roller and stick to the fabric or ground plate as compared to needle-less spinning.

6 Conclusions

Needleless electrospinning is a technique using electrical forces to tear and push spinning materials from free surface liquid toward electrode collector. Where as in the hollow needle, the polymer solution is moved ahead by mechanical forces. .Up to now, Nanospider is the unique commercial equipment to produce nanofibers-web via needleless electrospinning technology.This work includes parameter of needle and needleless electrospinning and then comparing with each other to find a relation.

From literature, it is obvious that polymer molecular weight and concentration of solution have significant effects on some dependent parameters of needle electrospinning such as fiber diameter and throughput. Once again, they play an important role in needleless electrospinning and strongly affect some dependent parameters of needleless electrospinning such as throughput and fiber diameter. The results of experiments show that throughput and fiber diameter increase with increasing polymer molecular weight and/or its concentration in solution.

- The higher is the viscosity of polymer solution (no matter whether caused by higher molecular weight or polymer concentration) the higher is the throughput (see Fig14,Fig 15)and higher fiber diameter(see Fig 13). Influence of Molecular weight and concentration is similar –throughput depends on viscosity and shows increase with increase in viscosity(see Fig 14) but in some range of molecular weight.(see Fig15)
- Conductivity of spinning solution affects strongly electrospinning dependent parameters, especially the throughput (see Fig 12,Fig 17).explained in the discussion part.As huge amount of ions are added in to solution with addition of NaCl-salt that causes a decrease in throughput for needle-less spinning.(see Fig12)

- PEO 100,000g/mol is non spinnable even if viscosity and conductivity is high enough. See (Fig 6,Fig 11). The PEO solution which didn’t spin on needle elctrospinning or giving electrospray ,did not spin in roller electro spraying too.(see Table12 and Fig 11)

- The fiber quality of needle electrospinning is better than needle-less electrospinning, and fiber diameter is less as compare to needleless electrospinning.(see Fig21-Fig 23)

- Adding NaCl-salt decreases the,Non-fibrous area and fiberdiameter distribution in both needle and needle-less electrospinning.(see , Fig22, Fig23)

- Fiber diameter distribution of needle-less electrospinning has more standard deviation as compared to needle electrospinning as explained in discussion part. (see Fig24-Fig29)

7 Future work

As Needle-less spinning is a new and time consuming process so to find more relatable parameters between both type of electrospinning different polymer solutions with different additives should be experimented to get a clear and strong relationship so that from the results of needle electrospinning it can be predicted about the behaviour of polymer solution at needle-less electrospinning.This research work is an initiative regarding the relationship between needle and needle-less electro spinning.

8 References

[1] S. Ramakrishna, K. Fujihara, W. Teo, T. Lim, and Z. Ma, An introduction to electrospinning and nanofibres, World Scientific Publishing Co., Singapor, 2005.

[2] M Anthony L.A, Science and Technology of Polymer Nanofibers; John Wiley & Sons, Inc., Hoboken, New Jersey, 2008

[3] M J. Stanger, N. Tucker, M. Staiger, Electrospinning, Rapra Technology, Report 190, ISSN: 0889-3144, 2005.

[4] O. Jirsak, F. Sanetrnik, D. Lukas, V. Kotek, L. Martinova, J. Chaloupek: EP 1673493

[5] M A.T. DAO and O. JIRSAK, Contribution to study of needless electrospinning mechanism, NANOFIBERS FOR THE 3RD MILLENNIUM – NANO FOR LIFE™ conference, Prague, CZ March 2009.

[6] M D.Lukas, A. Sarkar, L. Martinova, K. Vodsed'alkova, D. Lubasova et al. Physical principles of elctrospinning, Textile Progress Vol. 41, No.2, 2009

[7] Mckee MG, Wilkes GL, Colby RH, Long TE. Correlations of solution rheology with electrospun fiber formation of linear and branched polyesters. Macromolecules 2004;37:1760–7.

[8] Gupta P, Elkins C, Long TE, Wilkes GL. Electrospinning of linear homopolymers of poly (methylmethacrylate): exploring relationships between fiber formation, viscosity, molecular weight and concentration in a good solvent. Polymer 2005;46:4799–810.

[9] Jiang HL, Fang DF, Hsiao BS, Chu B, Chen WL. Optimization and characterization of dextran membranes prepared by electrospinning. Biomacromolecules 2004a;5: 326–33.

[10] Pham QP, Sharma U, Mikos AG. Electrospun poly (ε-caprolactone) microfiber and multilayer nanofiber/microfiber scaffolds: characterization of scaffolds and measurement of cellular infiltration. Biomacromolecules 2006;7:2796–805.

[11] Hayati I, Bailey AI, Tadros TF. Investigations into the mechanisms of electrohydrodynamic spraying of liquids. 1. Effect of electric-field and the environment on pendant drops and factors affecting the formation of stable jets and atomization. J Colloid Interface Sci 1987;117:205–21.

[12] Baumgarten PK. Electrostatic spinning of acrylic microfibers. J Colloid Interface Sci 1971;36:71–9.

[13] Zong X, Kim K, Fang D, Ran S, Hsiao BS, Chu B. Structure and process relationship of electrospun bioadsorbable nanofiber membrane. Polymer 2002;439:4403–12.

[14] Kim B, Park H, Lee SH, Sigmund WM. Poly (acrylic acid) nanofibers by electrospinning. Mater Lett 2005;59:829–32.

[15] Mit-uppatham C, Nithitanakul M, Supaphol P. Ultrafine electrospun polyamide-6 fibers: effect of solution conditions on morphology and average fiber diameter. Macromol Chem Phys 2004;205:2327–38.

[16] S. Megelski, J.S. Stephens, J.F. Rabolt and D.B. Chase, Macromolecules 35 (2002), pp. 8456–8466.

[17] A.M. Jamieson and D. Telford, Macromolecules 15 (1982), p. 1329.

[18] M.M. Hohman, M. Shin and G. Rutledge, Electrospinning and electrically forced jets,I, Stability theory, Physics of Fluids, 2001, 13, 8, 2201.

[19] Larrondo L, Manley RSJ. Electrostatic fiber spinning frompolymermelts. II. examination of theflowfield inan electrically drivenjet. J PolymSci, PolymPhys Ed 1981;19:921–32.

[20] Larrondo L, Manley RSJ. Electrostatic fiber spinning from polymer melts. III. Electrostatic deformation of a pendant drop of polymer melts. J Polym Sci, Polym Phys Ed 1981;19:933–40.

[21] Kumbar SG, Nukavarapu SP, James R, Hogan MV, Laurencin CT. Recent patents on electrospun biomedical nanostructures: an overview. Biomed Eng 2008;1:68–78.

[22] Demir MM, Yilgor I, Yilgor E, Erman B. Electrospinning of polyurethane fibers. Polymer 2002;43:3303–9.

[23] Yuan XY, Zhang YY, Dong CH, Sheng J. Morphology of ultrafine polysulfone fibers prepared by electrospinning. Polym Int 2004;53:1704–10.

[24] Reneker DH, Yarin AL, Fong H, Koombhongse S. Bending instability of electrically charged liquid jets of polymer solutions in electrospinning. J Appl Phys 2000;87:4531–47.

[25] Shin YM, Hohman MM, Brenner MP, Rutledge GC. Experimental characterization of electrospinning: the electrically forcedjet and instabilities. Polymer 2001;42:9955–67

[26] Doshi J, Reneker DH. Electrospinning process and applications of electrospun fibers. J Electrost 1995;35:151–6.

[27] Fong H, Liu WD, Wang CS, Vaia RA. Generation of electrospun fibers of nylon 6 and nylon 6-montmorillonite nanocomposite. Polymer 2002;43:775–80.

[28] Li D, Ouyang G, McCann JT, Xia Y. Collecting electrospun nanofibers with patterned electrodes. Nano Lett 2005;5:913–6.

[29] Jalili R, Morshed M, Abdolkarim S, Ravandi H. Fundamental parameters affecting electrospinning of PAN nanofibers as uniaxially aligned fibers. J Appl Polym Sci 2006;101:4350–7.

[30] Geng X, Kwon OH, Jang J. Electrospinning of chitosan dissolved in concentrated acetic acid solution. Biomaterials 2005;26:5427–32.

[31] William W.Graessley, Polymeric liquids & Networks, Published in 2008 by Taylor & Francis Group.

[32] Liu Y, He JH, Yu JY, Controlling numbers and sizes of beads in electrospun nanofibers, Polym Int 57:632–636 (2008)

[33] Choktaweesap N, Arayanarakul K, Aht-Ong D, Electrospun gelatin fibers: Effect of solvent system on morphology and fiber diameters, POLYMER JOURNAL 39-6 p622-631; 2007

[34] Wenguo C, Xiaohong L, Shaobing Z, J Weng, Investigation on Process Parameters of Electrospinning System through Orthogonal Experimental Design, Journal of Applied Polymer Science, Volume 103, Issue 5 (p 3105-3112).

[35] A.T DAO and O. Jirsak, The life of Jets in the roller electrospinning, 16th International Conference Strutex, Liberec Czech Republic, 3rd – 4th December 2009.

[36] Cengiz F; A.T DAO; O. Jirsak, Influence of solution properties on the roller electrospinning of poly(vinyl alcohol), Journal of Polymer Engineering and Science. (Accepted on 29th September 2009 in "Decision on PES-09-0035.R2").

[37] Lee E J, Dan K S and Kim B C 2006 Rheological Characterization of Shear-Induced Structural Formation in the Solutions of Poly(vinyl alcohol) in Dimethyl Sulfoxide J of Applied Polymer Science 101 465-71

[38] Graessley WW, Polymeric Liquids and Networks. Structure and Properties. Garland Science, NY and London 2004.

[39] L. da Vinci; The Notebooks of Leonardo da Vinci, (ed. And transl.) E. MacCurdy, Reynal and Hitchcock, New York, 1938.

[40] The Encyclopedia Americana; a library of universal knowledge. New York: Encyclopedia Americana Corp., 1918.

[41] J. Eggers and E. Villermaux, Physics of liquid jets, Reports on Progress in Physics, 71 (2008), pp. 1-79.

[42] D.H. Reneker and A.L. Yarin, Electrospinning jets and polymer nanofibres, Polymer, 49 (2008), pp. 2387-2425.

[43] Deitzel JM, Kleinmeyer J, Harris D, Beck Tan NC. The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer 2001;42(1):261–72.

[44] Theron SA, Zussman E, Yarin AL. Experimental investigation of the governing parameters in the electrospinning of polymer solutions. Polymer 2004;45(6):2017–30.

[45] Theron SA, Yarin AL, Zussman E, Kroll E. Multiple jets in electrospinning: experiment and modeling. Polymer 2005;46(9):2889–99.

[46] J.T. Kuikka, Scaling Laws in Physiology: Relationships between Size, Function, Metabolism and Life Expectancy, International Journal of Nonlinear Sciences and Numerical Simulation, 4 (2003), pp. 317-329.

[47] J-H. He, Y. Wu, W-W. Zuo; Critical length of straight jet in electrospinning; Polymer 46 (2005), 12637-12640.

[48] He JH, Wan YQ, Yu JY. Allometric scaling and instability in electrospinning. Int J Nonlinear Sci Numer Simul 2004;5(3):243–52.

[49] Shin YM, Hohman MM, Brenner MP, Rutledge GC. Experimental characterization of electrospinning: the electrically forced jet and instabilities. Polymer 2001;42(25):9955–67.

[50] Lukas D, Sarkar A, Pokornz P 2008 Self/Organization of Jets in Electrospinning From Free Liquid Surface. A Generalized Approach. J. of Applied Physics 103, 8, pp. 084309 1-7

[51] Ki CS, Baek DH, Gang KD, Lee KH, Um IC, Park YH. Characterization of gelatin nanofiber prepared from gelatin-formic acid solution. Polymer 2005;46:5094–102.

[52] Zhang C, Yuan X, Wu L, Han Y, Sheng J. Study on morphology of electrospun poly (vinyl alcohol) mats. Eur Polym J 2005;41:423–32.

[53] Dao Tuan thesis report,The role of rheological properties of polymer solutions in needle less electrostatic spinning,Liberec,2010

[54] Li D, Wang Y, Xia Y. Electrospinning nanofibers as uniaxially aligned arrays and layerby- layer stacked films. Adv Mater 2004;16:361–6.

[55] McKee, M. G., T. Park, S. Unal, I. Yilgor, and T. E. Long (2005). “Electrospinning of linear and highly branched segmented poly(urethane urea).” Polymer 46(7):2011–2015.

[56] F.E.Bailey and J.V.koleske,poly(ethylene oxide),Academic Press,Inc,NewYork, 1976

[57] Buchko CJ, Chen LC, Shen Y, Martin DC. Processing and microstructural characterization of porous biocompatible protein polymer thin films. Polymer 1999;40: 7397–407.